

WO 95-033782A1 is the international application of

[JP,95/033782,A1(1995)]

FULL CONTENTS CLAIM + DETAILED DESCRIPTION DRAWINGS

[Translation done.]

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Notes:

1. Untranslatable words are replaced with asterisks (* ** *).
2. Texts in the figures are not translated and shown as it is.

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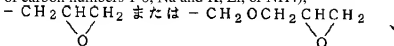
CLAIM + DETAILED DESCRIPTION

[Claim(s)]

1. it is the copolymer of the following (A) and (B) -- (A) -- 0.01 - 80mol %, and (B) -- 20 - 99.99mol % -- the fluorine polymer which contains and is characterized by number average molecular weights being 2000-20,000,000.

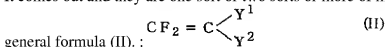
(A) is a general formula (I). : $\text{CH}_2=\text{CFCF}_2\text{-Rf}_1\text{-(CH}_2\text{)}_a\text{-X}_1$ (I)

the inside of [type, and X_1 - CH_2OH and - COOR_1 -- (-- here -- R_1 -- H, the alkyl group of carbon numbers 1-6, Na and K, Li, or NH_4).



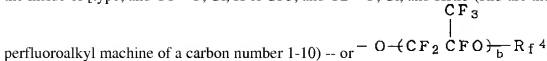
the alkylene group by which fluorine displacement of the carbon numbers 1-40 was carried out Rf_1 or - ORf_2 - (ether group by which fluorine displacement of the alkylene group by which fluorine displacement of the carbon numbers 1-40 was carried out Rf_2 , or the carbon numbers 3-50 was carried out), and a are the integers of 0, or 1-6 --]

It comes out and they are one sort or two sorts or more of monomers shown. (B) is a

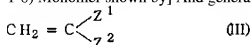


general formula (II). :

the inside of [type, and Y_1 -- F, Cl, H or CF_3 , and Y_2 -- F, Cl, and HRf_3 (Rf_3 are the

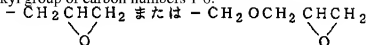


(b is the integer of 0, or 1-5, and Rf4 are the perfluoroalkyl machine of carbon numbers 1-6) Monomer shown by] And general formula (III) :



Z1 among [type The alkyl group of F, H, and carbon numbers 1-6, or the perfluoroalkyl machine of carbon numbers 1-10, Z2 is a monomer shown by the alkyl group of H, Cl, and carbon numbers 1-6, or -(CF2) d-Z3(d is integer of 1-10 and Z3 is F or H)]. They are one sort or two sorts or more of monomers chosen from the becoming group.

2. It is above (A) and Copolymer of (B) and (A) is 0.01 - 30Mol % (B), 70-99.99mol of ** % -- the fluorine polymer given in the 1st clause of a claim to contain.
3. (A) Given in 1st Clause of Claim, and (B) -- Further -- (C) -- [it is at Least One Sort of Copolymerizable Ethylene Nature Unsaturated Compound of Copolymers, and] The fluorine polymer 0.01 - 80mol %, and whose sum totals of (B) and (C) (A) is 20 - 99.99mol % and the number average molecular weights 2000-1,000,000.
4. Fluorine polymer given in the 1st clause of claim said X1 given is -CH2OH.
5. Fluorine polymer given in the 1st clause of claim said X1 given is -COOH.
6. Fluorine polymer given [said X1 given is -COOR1] in the 1st clause of claim R1 given is alkyl group of carbon numbers 1-6.

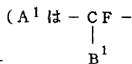
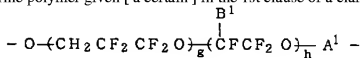


7. Said X1

It comes out and is a fluorine polymer given [a certain] in the 1st clause of a claim.

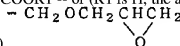
8. Aforementioned -Rf1- is -CF2-(CF2CF2) E. - (E is Integer of 0, or 1-10)

It comes out and is a fluorine polymer given [a certain] in the 1st clause of a claim.



9. Above - Rf1 -

or -CH2CF2- and B1, the integer of 0, or 1-5 and h are the integers of 0, or 1-10, and CF3 or F, and g are a= 0 -- X1 -CH2OH and -COOR1 -- or (R1 is H, the alkyl group of carbon



numbers 1-6, Na and K, Li, or NH4 here)

It comes out and is a fluorine polymer given [a certain] in the 1st clause of a claim.

10. [above (B) / be / it / Only Any One Sort of Tetrafluoroethylene or the Chlorotrifluoroethylene] or -- receiving the monomer sum total of (B) in either tetrafluoroethylene or chloro trifluoro CHIREN -- more than 30 mol % -- the fluorine polymer given in the 1st clause of a claim which contains and contains at least one or more sorts of other monomers.

11. the above (B) being one sort of vinylidene fluorides, or receiving the monomer sum

total of (B) in vinylidene fluoride -- more than 40 mol % -- the fluorine polymer given in the 1st clause of a claim which contains and contains at least one or more sorts of other monomers.

12. The fluorine polymer given in the 10th clause of a claim the given above (B) is only tetrafluoroethylene.

13. Above (B) Makes Either Tetrafluoroethylene or Chlorotrifluoroethylene

Indispensable, and They are Vinylidene Fluoride, Hexafluoro Propene, Hexafluoro

$$\text{CH}_2 = \underset{\substack{| \\ \text{Z}^3}}{\text{C}} (\text{CF}_2)_i \text{Z}^4$$

Isobutene, and Perfluoro Vinyl Ether as Other Monomers,

(-- the fluorine polymer given in the 10th clause of a claim the inside of a formula and Z3 given are the monomer mixtures containing at least one sort chosen from the group which consists of the fluorine-containing olefin H or F, and i are indicated to be for H or F, and Z4 by integer) of 1-10, ethylene, propylene, 1-butene, and isobutene.

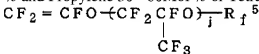
14. The fluorine polymer given in the 11th clause of a claim the given above (B) is only vinylidene fluoride.

Above (B) Makes Vinylidene Fluoride Indispensable and as Other Monomers 15.

Tetrafluoroethylene, The fluorine polymer given in the 11th clause of a claim which is the monomer mixture containing at least one sort chosen from the group which becomes from chlorotrifluoroethylene, hexafluoro propene, hexafluoro isobutene, and perfluoro vinyl ether.

16. Above (B) is Mixture Which Uses Either and Ethylene of Tetrafluoroethylene or Chlorotrifluoroethylene as Essential Ingredient, as opposed to the monomer sum total of (B) -- the monomer 0 of tetrafluoroethylene or chlorotrifluoroethylene 30 - 70mol % and ethylene 30 - 70mol % and others - 15mol % -- the fluorine polymer given in the 13th clause of a claim to include.

17. Monomer Mixture Which above (B) Becomes from Tetrafluoroethylene 40 - 70Mol % and Propylene 30 - 60Mol % or Tetrafluoroethylene 40 - 85Mol % and Type :



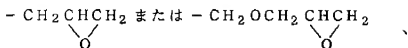
(-- the fluorine polymer given in the 13th clause of a claim which is the monomer mixture which consists of perfluoro vinyl ether 15 as which j is expressed with the integer of 0, or 1-5 among a formula, and Rf5 are expressed in perfluoroalkyl machine) of carbon numbers 1-6 - 60mol %.

18. (B) -- the vinylidene fluoride 70 - 99mol % and tetrafluoroethylene 1 - 30mol % of mixture; -- the vinylidene fluoride 50 - 99mol % -- 0-30mol of tetrafluoroethylene % and 1-20mol of chlorotrifluoroethylene% of mixture; or 60-99mol of vinylidene fluoride %, The fluorine polymer given in the 15th clause of a claim which is 0-30mol of tetrafluoroethylene % and 1-10mol of hexafluoropropylene% of mixture.

The fluorine polymer given in the 15th clause of a claim given 19. (B) is vinylidene fluoride 40 - 90mol %, tetrafluoroethylene 0 - % and hexafluoro 30mol propene 10 - 50mol% of a mixture.

20. General formula (IV): $\text{CH}_2=\text{CFCF}_2\text{-Rf}_6\text{-(CH}_2\text{)k-X}_2$ (IV)

The inside of [type and X2 are -CH2OH,

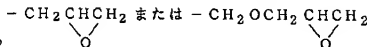


The alkylene group or -ORf7- (fluorine-containing ether group by which fluorine displacement of the fluorine-containing alkylene group by which fluorine displacement of the carbon numbers 1-40 was carried out Rf7, or the carbon numbers 3-50 was carried out) of carbon numbers 1-40 by which fluorine displacement was carried out Rf6, k is fluorine-containing olefin shown by] which is the integer of 0, or 1-6.

21. General formula (V): $\text{CH}_2=\text{CFCF}_2\text{-Rf8-(CH}_2\text{) m-COOR4 (V)}$

R4 among [type H, the alkyl group of carbon numbers 1-6, Na, K, The alkylene group or -ORf9- (ether group by which fluorine displacement of the alkylene group by which fluorine displacement of the carbon numbers 2-40 was carried out Rf9, or the carbon numbers 3-50 was carried out) of carbon numbers 3-40 by which fluorine displacement was carried out Li or NH4, and Rf8, m is fluorine-containing olefin shown by] which is the integer of 0, or 1-6.

22. Fluorine-containing olefin given in the 20th clause of a claim said X2 given is -CH2OH.

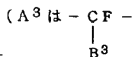
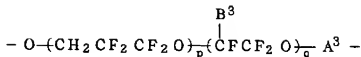


23. Said X2

It comes out and is fluorine-containing olefin given [a certain] in the 20th clause of a claim.

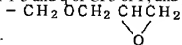
24. Aforementioned -Rf6- is -CF2-(CF2CF2) N, - (N is Integer of 0 or 1-10)

It comes out and is fluorine-containing olefin given [a certain] in the 20th clause of a claim.



25. Above -Rf6-

or -CH2CF2- and B3, the integer of 0, or 1-5 and q of CF3 or F, and p are the integers of



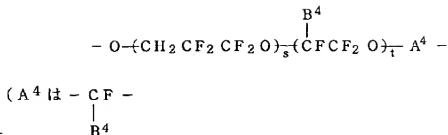
0 or 1-10, and k is 0 -- X2 -CH2OH -- or

It comes out and is fluorine-containing olefin given [a certain] in the 20th clause of a claim.

26. Fluorine-containing olefin given in the 21st clause of a claim said R4 given is H.

27. Fluorine-containing olefin given in the 21st clause of a claim said R4 given is NH4.

28. Fluorine-containing olefin given in the 21st clause of a claim aforementioned given -Rf8- is -CF2-(CF2CF2) r- (r is the integer of 1-10).



29. Above - Rf8 -

Or it is fluorine-containing olefin given [-CH₂CF₂- and B₄ are / the integer of 0, or 1-5 and given t of CF₃ or F, and s / the integers of 0, or 1-10 / B₄ given is CF₃ in the case of r=s=0] in the 21st clause of a claim given m is 0.

30.(D) It consists of a constituent obtained by mixing 1 to 99.9 weight % of heat-resistant thermoplastics which has 0.1 to 99 weight % of functional group content fluorine-containing polymer, a crystalline melting point beyond (E)150 degree C, or glass-transition temperature. The thermoplastics constituent which is at least one sort chosen from the group which this functional group content fluorine-containing polymer (D) becomes from a fluorine polymer given in the 1st clause of a claim.

31. said functional group content fluorine-containing polymer (D) was chosen from the group which consists of a fluorine polymer given in the 2nd clause of a claim -- at least --
 ** -- the thermoplastics constituent given in the 30th clause of a claim which is one sort.

32. The thermoplastics constituent given in the 31st clause of a claim with which said heat-resistant thermoplastics (E) was chosen from the group which consists of aromatic polyester, polycarbonate, polyamide, and poly arylene sulfide.

Said Functional Group Content Fluorine-containing Polymer (D) 33. Fluorine Polymer Given in 4th Clause of Claim, It is at least one sort chosen from the group which consists of a fluorine polymer given in the 6th clause of a claim, and a fluorine polymer given in the 7th clause of a claim. The thermoplastics constituent given in the 32nd clause of a claim with which heat-resistant thermoplastics (E) was chosen from the group which consists of aromatic polyester and polycarbonate and which is at least one sort.

Said Functional Group Content Fluorine-containing Polymer (D) 34. Fluorine Polymer Given in 5th Clause of Claim, And/or, the thermoplastics constituent given in the 32nd clause of a claim which was chosen from the group which consists of a fluorine polymer given in the 7th clause of a claim and it is at least one sort and heat-resistant given thermoplastics (E) is polyamide.

35. Said Functional Group Content Fluorine-containing Polymer (D) is at Least One Sort Chosen from Group Which Consists of a Fluorine Polymer Given in 4th Clause of Claim, and a Fluorine Polymer Given in 7th Clause of Claim. The thermoplastics constituent given in the 32nd clause of a claim heat-resistant given thermoplastics (E) is poly arylene sulfide.

36. The thermoplastics constituent given in the 33rd clause of a claim which is liquid crystal polyester with which said aromatic polyester has anisotropy at the time of fusion.

37. The thermoplastics constituent given in the 33rd clause of a claim said given functional group content fluorine-containing polymer (D) is a fluorine polymer given in the 16th clause of a claim.

38. The thermoplastics constituent given in the 33rd clause of a claim chosen from the group which said functional group content fluorine-containing polymer (D) becomes

from a fluorine polymer given in the 14th clause of a claim, and a fluorine polymer given in the 18th clause of a claim.

39. The thermoplastics constituent given in the 33rd clause of a claim which was chosen from the group which said functional group content fluorine-containing polymer (D) becomes from a fluorine polymer given in the 17th clause of a claim, and a fluorine polymer given in the 19th clause of a claim and which is fluorine-containing elastomer.

40. The thermoplastics constituent given in the 37th clause of a claim said given aromatic polyester is liquid crystal polyester.

41. The thermoplastics constituent given in the 38th clause of a claim said given aromatic polyester is liquid crystal polyester.

42. The thermoplastics constituent given in the 39th clause of a claim said given aromatic polyester is liquid crystal polyester.

43. Said functional group content fluorine-containing polymer (D) Thermoplastics constituent given in the 42nd clause of a claim which consists of 50 to 99.9 weight %, and 0.1 to 50 weight % of heat-resistant thermoplastics.

44. The thermoplastics constituent given in the 34th clause of a claim said given functional group content fluorine-containing polymer (D) is a fluorine polymer given in the 16th clause of a claim.

45. The thermoplastics constituent given in the 34th clause of a claim chosen from the group which said functional group content fluorine-containing polymer (D) becomes from a fluorine polymer given in the 14th clause of a claim, and a fluorine polymer given in the 18th clause of a claim.

46. The thermoplastics constituent given in the 34th clause of a claim which was chosen from the group which said functional group content fluorine-containing polymer (D) becomes from a fluorine polymer given in the 17th clause of a claim, and a fluorine polymer given in the 19th clause of a claim and which is fluorine-containing elastomer.

47. The thermoplastics constituent given in the 35th clause of a claim which was chosen from the group which said functional group content fluorine-containing polymer (D) becomes from a fluorine polymer given in the 17th clause of a claim, and a fluorine polymer given in the 19th clause of a claim and which is fluorine-containing elastomer.

48. Said functional group content fluorine-containing (polymer D) 0.1-40 weight % and heat-resistant thermoplastics (E) Thermoplastics constituent given in the 47th clause of a claim which consists of 60 to 99.9 weight %.

[Detailed Description of the Invention]

fluorine-containing olefin and a fluorine polymer -- and -- Thermoplastics constituent using the polymer Technical field This invention relates to the new functional group content fluorine polymer which keeps good relations with various heat-resistant thermoplastics well, and can form a uniform distributed state.

Furthermore, it is related with the new functional group content fluorine-containing olefin which can give the functional group of a functional group content fluorine polymer.

Furthermore, it is related with the thermoplastics constituent with which the mechanical property which consists of thermoplastics which has said functional group content fluorine polymer, a crystalline melting point of 150 degrees C or more, or glass-transition temperature, and chemical property have been improved.

Background art Polyacetal, polyamide, aromatic polyester, poly arylene sulfide, Since crystalline heat-resistant thermoplastics (these have a crystalline melting point of 150 degrees C or more), such as poly ketone and polyether ketone, polyamidoimide, and polyether nitrile, is excellent in a mechanical property and its moldability is moreover good Although used for the functional parts in fields, such as a car, an industrial machine, OA equipment, and electricity, an electric device, there is a more advanced market demand in chemical resistance, sliding nature, etc., and since these resin is generally brittleness, moreover, shock-proof improvement is desired especially. Moreover, polycarbonate, polyphenylene ether, polyarylate, Although the heat-resistant thermoplastics (these have the glass transition temperature of 150 degrees C or more) of amorphism nature, such as poly SARUHON and polyether sulphone, and polyether imide, is widely used for the use which harnesses transparency, dimensional stability, shock resistance, etc., Generally a problem is in chemical resistance, solvent resistance, and moldability.

On the other hand, they are polytetrafluoroethylene (PTFE), tetrafluoroethylene / perfluoroalkyl vinyl ether copolymer (PFA), Tetrafluoroethylene / hexafluoropropylene copolymer (FEP), Fluororesins, such as poly vinylidene fluoride (PVDF), and ethylene / tetrafluoroethylene copolymer (ETFE), a heat-resisting property, It excels in chemical resistance, solvent resistance, weatherability, sliding nature, plasticity, an electrical property, etc., and is widely used in fields, such as a car, an industrial machine, OA equipment, and electricity, an electric device. However, since it is inferior to a physical heat-resisting property as shown with a mechanical property or load deflection temperature compared with crystalline heat-resistant thermoplastics in many cases and dimensional stability is inferior compared with the heat-resistant thermoplastics of amorphism nature, the use range is limited.

reforming the fault of the heat-resistant thermoplastics of the aforementioned non-fluorine system by composite with fluorine-containing polymer (the thing of the shape of resin and the shape of an elastomer being included) **** -- reverse -- mainly Fluorine-containing resin-like polymer is reformed by composite with the heat-resistant thermoplastics of a non-fluorine system, and the trial which deals in a new material is performed briskly.

First, it is an example which carries out a fusion blend simply with a kneading machine. For example, adding commercial fluorine-containing elastomer for the purpose which improves shock resistance, crack resistance, and thermal shock hardness without spoiling a heat-resisting property, chemical resistance, etc. which are the feature of poly arylene sulfide is indicated by JP,S57-202344,A. Moreover, it is at JP,H1-165647,A and JP,H2-110156,A, A coefficient of linear expansion is reduced without spoiling the weatherability of fluorine-containing polymer, such as PVDF, chemical resistance, abrasion resistance, and resistance to contamination, and addition of the polymer (aromatic polyester etc.), i.e., liquid crystallinity polymer, which forms an anisotropic melt phase is performed in order to improve mechanical physical-properties and shaping workability further. There are JP,H4-5693,B and JP,S63-230756,A as an example of a blend of liquid crystallinity polymer and PTFE. In JP,S50-7850,A, it is indicated that the blend of PVDF is effective for the absorptivity of polyamide and a hygroscopic improvement.

Furthermore, fibrous strengthening agents and talcs, such as glass fiber and wollastonite,

The example which improved the mold-release characteristic from a metal pattern by blending a fluorine system polymer with the aromatic series poly SARUHON constituent which blended inorganic fillers, such as a glass bead, and reduced molding shrinkage is indicated to JP,S60-23448,A.

Moreover, to various synthetic resins, PTFE powder is blended and, generally the trial which improves sliding characteristics is performed widely.

However, since fluorine-containing polymer has small surface energy, generally there is a problem that compatibility with other material is scarce. Therefore, it is although phase separation will be produced if the fusion blend of fluorine-containing polymer and the other material is carried out, The interface adhesive strength was equal to there being nothing substantially, and it was difficult to be hard to distribute fluorine-containing polymer in other material also during a blend, while exfoliation of an interface occurs easily, to cause condensation, and to fully demonstrate the addition effect.

In order to raise the compatibility of the different-species polymer which are such faults, adding what is called a compatibilizer as the 3rd component is often performed. In order to improve the shock resistance in JP,S62-218446,A, without spoiling the flowability of poly arylene sulfide The more effective thing is described, if the constituent which blended thermoplastic fluorine-containing elastomer is indicated and fluoro aliphatic series machine content polymer is added in this gazette for compatibility improvement. Moreover, at JP,H3-62853,A, it is poly arylene sulfide, When blending the thermoplastics containing PVDF, the method of adding as a compatibilizer the graft polymer which consists of the vinyl polymerization object, methyl methacrylate polymer, or the acrylonitrile / styrene copolymer which has an epoxy group is indicated.

Moreover, in Claim 2, aforementioned JP,H1-197551,A, and aforementioned JP,H1-263144,A of JP,H1-165647,A, the blend of PVDF and anisotropic melt phase formation nature polymer is received, It is said that addition of acrylic polymer, polyvinyl acetate, and polyvinyl methyl ketone is more effective than a simple blend respectively.

In JP,S64-11109,A, either of N-vinyl pyrrolidone or methyl (meta) acrylate, As a compatibilizer [as opposed to the blend of polyamide and PVDF for the block polymer which consists of any one sort of an ethylene system unsaturation monomer, a polycondensation monomer, or lactam] The example to be used is indicated.

Moreover, on the occasion of polyphenylene ether and the blend of fluorine-containing polymer like PVDF, it uses that polyphenylene ether, polystyrene and PVDF, and acrylic polymer are respectively excellent in compatibility for JP,H1-98650,A and JP,H1-110550,A. Using as a compatibilizer the copolymer which consists of polystyrene and acrylic polymer is indicated.

However, probably because the carbon number of the fluoro aliphatic series machine in the compatibilizer in JP,S62-218446,A is 20 or less thing of a low degree of polymerization, the effect of compatibility improvement is inadequate. Moreover, in other gazettes, it is an example using the non-fluorine system compatibilizer substantially compounded altogether using the compatibility of PVDF and carbonyl group content polymer like acrylic polymer being excellent, and fluorine-containing polymer is limited to PVDF. Moreover, by the compatibility improvement method using such a compatibilizer, since a compatibilizer's own chemical resistance and own heat-resisting property are inferior to the polymer of a principal component, there is a problem that the physical properties of mold goods fall.

Moreover, the trial which improves the dispersibility of the constituent which consists of fluorine-containing polymer and thermoplastics what is called by dynamic vulcanization also occurs. In JP,H3-185042,A, the blend of the thermoplastic polymer which has fluorine-containing elastomer in which bridging is possible, a crystalline melting point of 150 degrees C or more, or glass transition temperature is faced. By vulcanizing fluorine-containing elastomer during a fusion blend, it is indicated that the dispersibility of fluorine-containing elastomer improves and a thermoplastic elastomer is obtained. JP,H3-172352,A also used the dynamic vulcanizing method for the shock-proof improvement by fluorine-containing elastomer of a polyphenylene sulfide, and has attained the micro-disperse of fluororubber.

However, by these dynamic vulcanizing methods, vulcanization of fluorine-containing elastomer is blending fusion with other material, and is performed, the impurity based on the vulcanizing agent and other additives which are used by the usual vulcanization technique remains into a constituent, and there is a problem that character, such as the chemical resistance of mold goods, deteriorates.

Moreover, since, especially as for the dynamic vulcanization constituent which consists of thermoplastics and fluorine-containing elastomer, thermoplastics serves as a matrix, the chemical resistance of a constituent etc. tends to be governed by the characteristics of thermoplastics, and the effect by addition of fluorine-containing elastomer is inadequate. On the other hand, there is also a report using reactant functional group content fluorine-containing polymer of a constituent. JP,63-105062,A No., a JP,63-254155,A number, and JP,63-264672,A No. -- each gazette There is an example of a blend of the fluoropoly ether which introduced the functional group into the end, the polymer, functional group content fluorine-containing elastomer containing a functional group and the poly fluoro alkyl group of carbon numbers 2-20, etc. and matrix polymer. However, each of these is while two kinds of functional group content polymer distributes in matrix polymer.

Network structure is formed in response to mutual, it is the mechanism of combining this network structure and matrix polymer physically, and chemical compatibility or reactivity with matrix polymer are not used directly.

Therefore, the combination of two or more sorts of functional groups which certainly react mutually is required, and they must prepare the conditions which form network structure. Moreover, usually fluoropoly ether is obtained as an oil-like substance, and is also expensive, and the addition effect is only a limited thing that is called a lubricative improvement of matrix polymer. The thing of the low molecular weight which cannot specify easily the polymer which furthermore contained the poly fluoro alkyl group as polymer, either is illustrated.

Moreover, vinyl, an allyl compound, acrylate, alkoxysilane, amide, sulfonate, pyridine, and a substituent like carboxylate JP,H5-112612,A has a description about the introduced property modification fluoro hydrocarbon polymer. Especially in these substituents, the thing of an amide group is guided to an amino group, and the thing of carboxylate is further guided to a carboxyl group, and it is indicated that a graft can be carried out to aromatic polyamide or aromatic polyester. Moreover, the graft thing is used for the blend with commercial engineering polymer, and it is said that a surface property, weatherability, abrasion resistance, and absorptivity are improved. however, the double bond formed in the vinylidene system polymer after the substituent of this property modification polymer performed the deHF reaction of the vinylidene

system polymer -- the reactant high nucleophilicity atom Y (an amino group --) It is a polymer reaction about Y-R-Z which doubles and has an oxy-group, a thio machine, and said property modification nature substituent Z through the joint segment R. It has obtained.

That is, since it is a polymer reaction, it is hard to introduce a functional group uniformly, therefore presentation distribution is produced to functional group concentration, and it is hard to acquire effect sufficient at the time of the blend with thermoplastics for dispersibility and compatibility.

Moreover, a reaction reagent remains at the time of a hydrolysis of the time of property modification substituent introduction, amide, or carboxylate, and a heat-resisting property and chemical resistance are reduced. Moreover, the heat-resisting property of polymer itself [which was obtained since the joint segment of a property modification reagent was a high draw carbon system] becomes weak in the portion, a kneading time solution is carried out at heat-resistant thermoplastics and high temperature, and the physical properties of the obtained blend thing are reduced.

Moreover, the deHF reactant of a vinylidene system polymer has remarkable coloring, and spoils the appearance of mold goods remarkably. Moreover, the effect of improvement in dispersibility fluorine-containing polymer is restricted to a vinylidene fluoride system polymer, and difficult introduction of a hydroxy group and a glycidyl group and sufficient by this method for the blend with aromatic polyester, polycarbonate, and a polyphenylene sulfide is not acquired. Moreover, there is no detailed description of the example of a blend constituent with heat-resistant thermoplastics and the physical properties at the time of a blend here.

In the thermoplastic elastomer composition of JP,S63-81159,A, it is indicated by by denaturalizing fluororubber by the carboxyl group, the hydroxy group, or an epoxy group in the case of the blend with polyether ester amide and fluororubber that a mechanical property is improved.

However, by being based on copolymerization of a fluorine monomer and the acrylic monomer containing a functional group, and introducing a functional group, the functional group content fluororubber shown here reduces a heat-resisting property and chemical resistance, and reduces the physical properties of mold goods by the blend with heat-resistant thermoplastics. Copolymeric [which make tetrafluoroethylene and vinylidene fluoride representation / the fluorine monomer and copolymeric] produce presentation distribution that it is bad and hard to obtain uniform functional group concentration for every polymer molecule, and the functional group content acrylic monomer cannot acquire effect sufficient at the time of the blend with thermoplastics for dispersibility and compatibility easily. Moreover, generally polyether ester amide has low chemical resistance compared with polyamide resin.

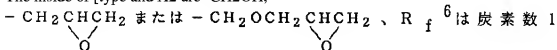
As mentioned above, when blending fluorine-containing polymer and thermoplastics, fluorine-containing polymer reduces the physical properties of moldings using [generally, since compatibility is scarce, it is difficult to deal in the blend whose characteristics were stable, and] it. Moreover, although examination of various additives, the property modification of a fluororesin, and denaturation are tried for compatibility improvement, the constituent of the fluorine-containing polymer and the fluorine-containing polymer to which a heat-resisting property, chemical resistance, etc. of a constituent are not reduced, and thermoplastics is not obtained.

The purpose of this invention offers new functional group content fluorine-containing olefin for dealing in the new functional group content fluorine polymer which keeps good relations with various heat-resistant thermoplastics well, and can form a uniform distributed state, and its fluorine polymer.

further -- in addition, the compatibility of an interface is improved with the blend with this functional group content fluorine polymer and various heat-resistant thermoplastics, and the thermoplastics constituent which can give a mechanical property, moldability, the outstanding heat-resisting property, and outstanding chemical resistance to mold goods is offered.

Indication of invention Functional group content fluorine-containing olefin of this invention is a general formula (IV). : $\text{CH}_2=\text{CFCF}_2\text{-Rf}_6\text{-(CH}_2\text{)k-X}_2$ (IV)

The inside of [type and X_2 are $-\text{CH}_2\text{OH}$,



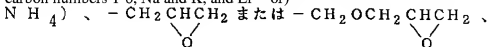
The alkylene group or $-\text{ORf}_7$ which is -40 and by which fluorine displacement was carried out - (fluorine-containing ether group by which fluorine displacement of the fluorine-containing alkylene group by which fluorine displacement of the carbon numbers 1-40 was carried out Rf_7 , or the carbon numbers 3-50 was carried out) k is] which is the integer of 0, or 1-6, or a general formula (V). : $\text{CH}_2=\text{CFCF}_2\text{-Rf}_8\text{-(CH}_2\text{)m-COOR}_4$ (V)

As for the inside of [type, and R_4 , H, the alkyl group of carbon numbers 1-6, Na and K, Li or NH_4 , and Rf_8 are the alkylene group or $-\text{ORf}_9$ of carbon numbers 3-40 by which fluorine displacement was carried out (ether group by which fluorine displacement of the alkylene group by which fluorine displacement of the carbon numbers 2-40 was carried out Rf_9 , or the carbon numbers 3-50 was carried out), m is shown by] which is the integer of 0, or 1-6.

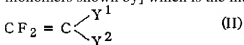
The functional group content fluorine polymer of this invention is a copolymer of following (A) and (B), and (A) is 0.01 - 80mol % (B), 20-99.99mol of ** % -- it contains and is characterized by number average molecular weights being 2000-20,000,000.

(A) is a general formula (I). : $\text{CH}_2=\text{CFCF}_2\text{-Rf}_1\text{-(CH}_2\text{)a-X}_1$ (I)

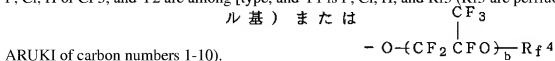
the inside of [type, and X_1 $-\text{CH}_2\text{OH}$ and $-\text{COOR}_1$ (here -- R_1 -- H, the alkyl group of carbon numbers 1-6, Na and K, and Li -- or)



Rf_1 is the alkylene group or $-\text{ORf}_2$ of carbon numbers 1-40 by which fluorine displacement was carried out. - (ether group by which fluorine displacement of the alkylene group by which fluorine displacement of the carbon numbers 1-40 was carried out Rf_2 , or the carbon numbers 3-50 was carried out) a is one sort or two sorts or more of monomers shown by] which is the integer of 0, or 1-6, and (B) is a general formula (II). :

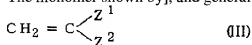


F, Cl, H or CF₃, and Y₂ are among [type, and Y₁ is F, Cl, H, and Rf₃ (Rf₃ are perfluoro
ル基) または



(b is the integer of 0, or 1-5, and Rf₄ are the perfluoroalkyl machine of carbon numbers 1-6)

The monomer shown by], and general formula (III) :



The inside of [type and Z₁ are the alkyl groups to F, H, and carbon numbers 1-6. Or the perfluoroalkyl machine of carbon numbers 1-10 and Z₂ are one sort or two sorts or more of monomers chosen from the group which consists of a monomer shown by the alkyl group of H, Cl, and carbon numbers 1-6, or -(CF₂) d-Z₃(d is integer of 1-10 and Z₃ is F or H)].

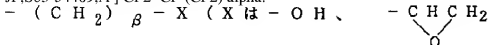
The thermoplastics constituent of this invention is (D) functional group content fluorine-containing polymer. It consists of 1 to 99.9 weight % of heat-resistant plasticity resin which has at least one-sort the crystalline melting point or glass-transition temperature 0.1 to 99 weight %, and beyond (E)150 degree C chosen from said functional group content fluorine polymer.

It explains in order of hereafter.

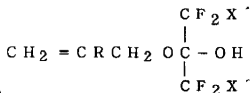
Functional group content fluorine-containing olefin which is invention of the 1st of this invention is related with the new functional group content fluorine-containing olefin which can give a hydroxy group, a glycidyl group, a carboxyl group, and a carboxylate machine to a fluorine polymer.

The most general thing as a comonomer which gives the same functional group to a polymer, Although the vinyl ether represented with the compound of an acrylate system or (meta) an acrylic acid system, or hydroxyalkyl vinyl ether and a glycidyl vinyl yell with a hydroxy group, a glycidyl group, and a carboxyl group (meta) is known the functional group content unsaturated compound of these high draw carbon system -- fluoro olefin (tetrafluoroethylene --) Copolymeric [with the olefin represented by vinylidene fluoride, chlorotrifluoroethylene, etc.] is inadequate, or it has the fault in which the heat-resisting property of the copolymer obtained even if copolymerization was possible, and chemical resistance are reduced remarkably.

It is [in / as functional group content fluorine-containing olefin / on the other hand / JP,S63-54409,A] CF₂=CF-(CF₂) alpha.



Or although there is a report about the compound shown by -COOH, copolymeric [of fluoro olefin] is inadequate, and in order to reduce a rate of polymerization and to deal in the copolymer which has a predetermined presentation, a lot of preparations are needed.



In JP,S50-143888,A

Hemiacetal compounds [R / (/ ' / H or methyl, and / X), such as F or Cl), Although the partial fluorine substituted compound CH₂=CH-Rf-CH₂CH₂Y (the divalent organic group and Y by which fluorine displacement of Rf was carried out are CH₂OH, COOH, and others) is indicated in the Patent Publication table Taira No. 503104 [five to] gazette, In the polymer [these] using a monomer, it is in a polymer principal chain.

H
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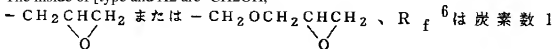
A heat-resisting property falls and it has the fault which deteriorates easily especially at high temperature. Moreover, as for said hemiacetal compound, copolymeric [with a fluorine monomer] is bad, and it is difficult to carry out especially polymer quantification.

In JP,S58-85832,A and the Patent Publication table Taira No. 503935 [five to] gazette, it is a perfluoro vinyl ether group. There is a description of the hydroxy content fluorine-containing olefin which it has, and USP4,209,635 have a description of carboxylate machine content fluorine-containing olefin with a perfluoro vinyl ether group. The CF₂=CFO-machine in these fluorine-containing olefin should receive an alkaline medium. [the hydroxy group content fluorine-containing olefin which is weak and has especially a perfluoro vinyl ether group] In the environment of acidity (PKa is seven or more) lower than the acidity (PKa⁵⁻⁶) of the hydroxy group, the ⁵⁻⁶-ized reaction of vinyl ether itself, and a gay polymerization (fluorine-containing polyether generates) and the hydrolysis reaction of a vinyl ether group occur easily. therefore -- for example, since a rate of polymerization falls on condition of a weak alkali - alkalinity or the introduction amount to the copolymer of vinyl ether falls in the case of copolymerization in a basin system medium with other ethylene nature unsaturated compounds, polymerization conditions cannot be chosen widely. Moreover, since its synthetic pathway is complicated, it is expensive, and the perfluoro vinyl ether compound with these functional groups is economically disadvantageous when producing industrially. The purpose of this invention cancels said fault and offers the new functional group content fluorine-containing olefin which can give a functional group to a fluorine polymer. It is copolymerization with more detailed ⁵⁻⁶ [to which a rate of reaction is not remarkably reduced with ⁵⁻⁶ ethylene nature unsaturated compound especially a fluorine-containing ethylene nature unsaturated compound, and good copolymerization reactivity] fluorine-containing ethylene nature unsaturated compound. The synthetic process for dealing in the functional group content fluorine-containing olefin of ⁵⁻⁶ this invention itself to which the thermal stability of the copolymer obtained and chemical stability are not reduced has the feature of being possible, comparatively easily and industrially. The new fluorine-containing olefin which can introduce a reactant high functional group into a fluorine polymer can be offered.

The 1st is a general formula (IV) which has a hydroxy group or a glycidyl group as a

functional group of functional group content fluorine-containing olefin of this invention. :
 $\text{CH}_2=\text{CFCF}_2\text{-Rf}_6\text{-(CH}_2\text{)}_k\text{-X}_2$ (IV)

The inside of [type and X_2 are $-\text{CH}_2\text{OH}$,



- the alkylene group by which fluorine displacement of 40 was carried out or $-\text{ORf}_7-$ (ether group by which fluorine displacement of the alkylene group by which fluorine displacement of the carbon numbers 1-40 was carried out Rf_7 , or the carbon numbers 3-50 was carried out), and k are fluorine-containing olefin shown by] which is the integer of 0, or 1-6.

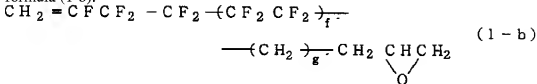
In fluorine-containing olefin of a general formula (IV), as for the structure of Rf_6 , one is the alkylene group by which fluorine displacement of the carbon numbers 1-40 was carried out, and the shape of a normal chain, branched state, or its mixture is also contained.

The example of representation desirable in it is a formula (1). : $\text{CH}_2=\text{CFCF}_2\text{-(CF}_2\text{CF}_2\text{)}_{a'}\text{-(CH}_2\text{)}_{b'}\text{-X}_3$ (1)

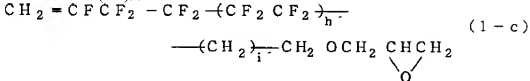
[-- the inside of a formula, and X_3 -- said X_2 and b' -- said k -- the same -- a' is fluorine-containing olefin shown by integer] of 0, or 1-10.

The still more desirable example of representation is a formula (1-a). : $\text{CH}_2=\text{CFCF}_2\text{-(CF}_2\text{CF}_2\text{)}_{d'}\text{-(CH}_2\text{)}_{e'}\text{-CH}_2\text{OH}$ (1-a)

(-- the inside of a formula, the integer of d' , or 1-10, and e' -- integer) of 1-5, and formula (1-b):



They are (the integer of the inside of a formula, the integer of f' , or 1-10, g' , or 1-6), and a formula (1-c). :



(As for inside of formula, and h' , the integer of 0, or 1-10 and i' are the integers of 1-5)

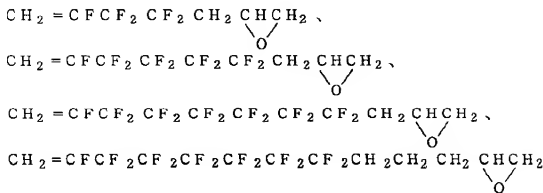
It comes out and is fluorine-containing olefin expressed.

Formula The desirable example of the fluorine-containing olefin shown by (1-a)

$\text{CH}_2=\text{CFCF}_2\text{CF}_2\text{CH}_2\text{CH}_2\text{OH}$, $\text{CH}_2=\text{CFCF}_2\text{CF}_2\text{CF}_2\text{CF}_2\text{CH}_2\text{CH}_2\text{OH}$,

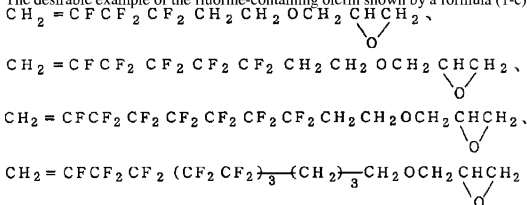
$\text{CH}_2=\text{CFCF}_2\text{CF}_2\text{CF}_2\text{CF}_2\text{CF}_2\text{CH}_2\text{CH}_2\text{OH}$, and $\text{CH}_2=\text{CFCF}_2\text{CF}_2\text{-(CF}_2\text{CF}_2\text{)}_3\text{-(CH}_2\text{)}_3\text{-CH}_2\text{OH}$ etc. is raised.

The desirable example of the fluorine-containing olefin shown by a formula (1-b)



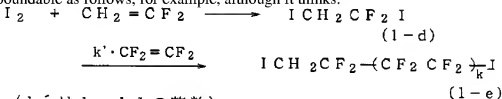
**** is raised.

The desirable example of the fluorine-containing olefin shown by a formula (1-c)



**** is raised.

Various the synthetic methods of fluorine-containing olefin of a formula (1) are compoundable as follows, for example, although it thinks.



First, (k' は 1 ~ 11 の整数)

After carrying out the addition reaction of the iodine to vinylidene fluoride, it can deal in (1-e) by carrying out the TEROMERI reaction of the bottom tetrafluoroethylene of existence of a radical initiator.

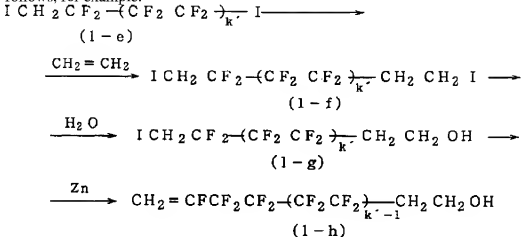
The reaction of the compound type (1-d) and tetrafluoroethylene which added iodine to vinylidene fluoride, 200 degrees C of reaction temperature is 40-100 degrees C preferably from a room temperature under existence of radical initiators, such as peroxide and an azo compound. It can deal in (1-e) by reacting tetrafluoroethylene under bubbling or the pressurization not more than 15 kgf/cm²G by ordinary pressure, keeping desirable ordinary pressure or the pressurization state not more than 5 kgf/cm²G.

As peroxide, they are t-butyl peroxy i-butyrate and tert-butyl peroxide (2-ethylhexanoate), Azobisisobutyronitril etc. can be illustrated as azo compounds, such as i-BUCHIRIRU peroxide, G i-propylperoxy dicarbonate, and di-n-propyl peroxi

dicarbonate. They are [whether a solvent is used and] R-113, R-114, and R-141b, for example, Chlorofluorocarbon system solvents, such as R-115; aromatic series system solvents, such as hydrocarbon system solvent; benzene, such as chlorine-based solvent; hexane, such as carbon tetrachloride, KUROROHOMU, and a methylene chloride, and cyclohexane, and toluene, etc. can be adopted, and especially a chlorofluorocarbon system solvent is desirable.

The compound of the obtained formula (1-e) is used as a starting material, and the compound of a formula (1-a) with a hydroxy group, a formula (1-b) with a glycidyl group, and a formula (1-c) with a glycidyl ether machine can be compounded, respectively.

Fluorine-containing olefin with a hydroxy group of a formula (1-a) is compoundable as follows, for example.



that is, bottom ethylene of existence of a radical initiator is reacted to the compound of a formula (1-e) -- making (1-f) -- carrying out a deIF reaction using metals, such as Zn, after obtaining, making near iodine and the water which subsequently introduced ethylene react and making it convert into -OH group It can deal in hydroxy content fluorine-containing olefin.

The reaction of (1-e) and ethylene is the bottom of existence of radical initiators, such as peroxide and an azo compound, or UV irradiation, Usually, 20-200 degrees C, 50-100 degrees C of this better foil, and ethylene can be dealt in the compound of a formula (1-f) ordinary pressure - 50 kgf/cm²G, and by making it react, keeping desirable ordinary pressure or the pressure not more than 10 kgf/cm²G.

As the above-mentioned peroxide, they are tert-butyl peroxide i-butyrate and tert-butyl peroxide (2-ethylhexanoate), Azobisisobutyronitril etc. can be illustrated as azo compounds, such as i-BUCHIRIRU peroxide, G i-propylperoxy dicarbonate, and di-n-propyl peroxi dicarbonate. The same thing as the TEROMERI-ized reaction of tetrafluoroethylene of a solvent is desirable.

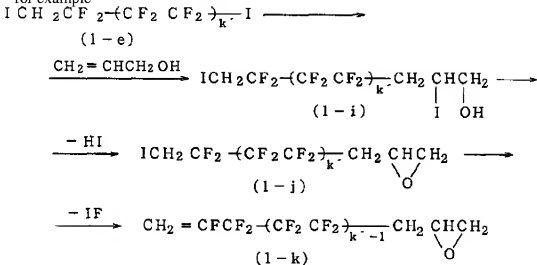
The hydroxylation reaction of the iodine atom by the side of ethylene introduction of the obtained ethylene addition product type (1-f) can take various methods. For example, the method to which chlorosulphonic acid and water are made to react in order or the method on which H₂O is made to act in DMF shown in JP,S52-8807,B, the method on which H₂O is made to act in the dimethyl sulfoxide shown in JP,H2-28585,B, etc. can be used. Furthermore, a compound (1-g) can be dealt in the target hydroxy group content fluorine-

containing olefin compound (1-h) by a deIF reaction among a polar solvent using dehalogenation agents, such as zinc.

The solvents in this reaction are ether system solvents, such as mono-glyme, a jig lime, and dioxane, for example, Ketone solvent, such as alcoholic solvent, such as methanol and ethanol, acetone, and MEK, water, DMF, etc. are used preferably, and methanol, a jig lime, etc. are still more desirable solvents.

Although a general dehalogenation agent is used for a deIF reaction and magnesium, tin, copper, iron, sodium, manganese, etc. other than zinc are raised, zinc and magnesium are desirable at the relation of a rate of reaction. 20-150 degrees C of reaction temperature is 40-80 degrees C preferably. The amount of the dehalogenation agent used is 1.02 to 3 times preferably 1.0 to 5 times in a molar ratio to a compound (1-g). As for the reaction method, it is desirable to add zinc dust to a solvent, to warm, after agitating and distributing, and for a compound (1-g) to be slowly dropped in the state, and to make a reaction complete.

how to compound fluorine-containing olefin of a compound (1-b) with a glycidyl group -
- for example



That is, after making bottom allyl alcohol of existence of a radical initiator react to the compound of a compound (1-e) and obtaining a compound (1-i), it deHI(s) in a base and an epoxy ring is formed. Subsequently, it can deal in glycidyl group content fluorine-containing olefin by carrying out a deIF reaction using metals, such as Zn. The reaction of a compound (1-e) and allyl alcohol, 20-200 degrees C of reaction temperature can be preferably attained by making it react at 50-150 degrees C under existence of radical initiators, such as peroxide same with having used at the reaction with tetrafluoroethylene or ethylene and an azo compound.

By next making (1-i) react with a somewhat superfluous base, it deHI(s) and can deal in the compound of the compound (1-j) in which the epoxy ring was formed. A base Hydroxides, such as sodium hydroxide, potassium hydroxide, and a calcium hydroxide, Alkali metal carbonate, such as sodium carbonate and sodium hydrogencarbonate, sodium methoxide, In order to prevent the epoxy ring which tertiary amine, such as metal alkoxide, such as sodium ethoxide and potassium t-butoxide, triethylamine, and pyridine, was desirable, and they generated carrying out ring breakage **, sodium hydroxide,

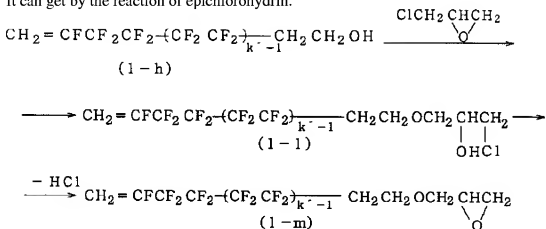
potassium hydroxide, a calcium hydroxide, alkali metal carbonate, and tertiary amine are still more desirable.

When reacting even if there is no solvent, but using it For example, alcoholic solvent, such as water, methanol, and ethanol, tetrahydrofuran, Ether system solvents, such as dioxane, mono-glyme, and a jig lime, acetone, In order to prevent the generated epoxy ring carrying out ring breakage although tertiary amine system solvents, such as ketone solvent, such as methyl ethyl ketone and methyl isobutyl ketone, triethylamine, and pyridine, dimethylformamide, dimethyl sulfoxide, etc. are desirable A **** solvent or when using it, an ether system, a ketone system, a tertiary amine system solvent, dimethylformamide, dimethyl sulfoxide, etc. are still more desirable.

Although the deIF reaction of the obtained compound (1-j) can be performed like the deIF reaction of a compound (1-g) using metals, such as Zn, you should avoid, also in order to prevent the generated epoxy ring carrying out ring breakage of the alcoholic solvent, such as water, methanol, and ethanol, as a solvent.

Various the methods of compounding fluorine-containing olefin of a compound (1-c) with a glycidyl ether machine are fluorine-containing olefin (1-h) which has a hydroxy group although it thinks.

It can get by the reaction of epichlorohydrin.



For example, although Lewis acid system acid catalysts, such as $\text{BF}_3(\text{C}_2\text{H}_5\text{OC}_2\text{H}_5)_3$ and SnCl_4 , can be used, $\text{BF}_3(\text{C}_2\text{H}_5\text{OC}_2\text{H}_5)_3$ are desirable, and they make an acid catalyst act on a compound (1-h) and epichlorohydrin, a compound (1-l) is made to generate, and it is a base. By a deHCl reaction, it can deal in a compound (1-m). reaction temperature -10 degrees C - 200 degrees C are 0-100 degrees C preferably. Even if it does not use a solvent Although it is good, for example Ether system solvents, such as mono-glyme, a jig lime, dioxane, and tetrahydrofuran, Although chlorofluorocarbon system solvents, such as chlorine-based solvents, such as hydrocarbon system solvents, such as ketone solvent, such as acetone and MEK, hexane, and cyclohexane, chloroform, dichloromethane, and carbon tetrachloride, R-113, and 141b, 115, etc. are desirable, an ether system solvent is still more desirable.

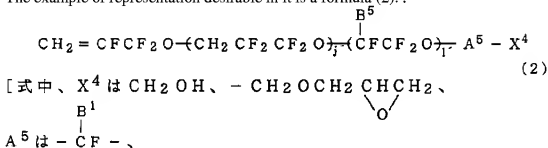
It can deal in the deHCl reaction of a compound (1-l) by the method same with dealing in the compound of a compound (1-j) by deHI by the base of the above-mentioned compound (1-i).

Moreover, also in the reaction of a compound (1-h), epichlorohydrin more than an

equivalent, and a base, a compound (1-m) is compoundable. As a base, sodium hydroxide, potassium hydroxide, sodium hydride, etc. are desirable. 20-200 degrees C of reaction temperature is 50-150 degrees C preferably. Even if it does not use a solvent Although it is good, for example Ether system solvents, such as mono-glyme, a jig lime, dioxane, and tetrahydrofuran, Although chlorofluorocarbon system solvents, such as chlorine-based solvents, such as hydrocarbon system solvents, such as ketone solvent, such as acetone and MEK, hexane, and cyclohexane, chloroform, dichloromethane, and carbon tetrachloride, R-113, and 141b, 115, etc. are desirable, a non-solvent or an ether system solvent is still more desirable.

In fluorine-containing olefin of a general formula (IV), another structure of Rf6 is an ether group shown by -ORf7-. -Rf7 are the ether group by which fluorine displacement of the alkylene group by which fluorine displacement of the carbon numbers 1-40 was carried out, or the carbon numbers 3-50 was carried out, and the shape of a normal chain, branched state, or those mixtures are also contained.

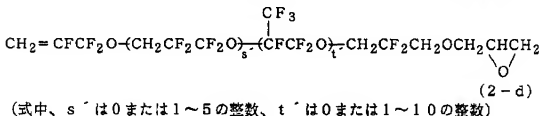
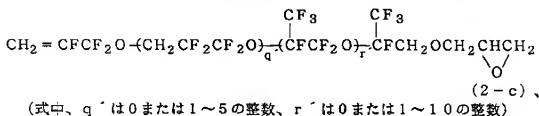
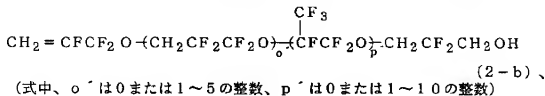
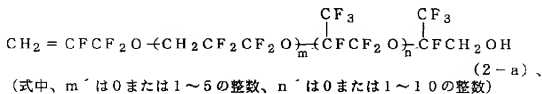
The example of representation desirable in it is a formula (2). :



Or as for CF3 or F, and j', in -CH2CF2- and B5, the integer of 0, or 1-5 and 1' are integer [of 0, or 1-10]].

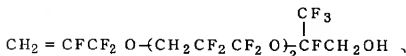
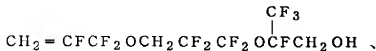
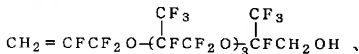
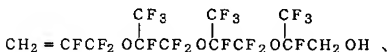
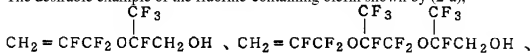
It comes out and is fluorine-containing olefin shown.

the still more desirable example of representation -- a compound (2-a), (2-b), and (2-c) (2-d) :



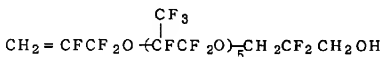
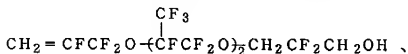
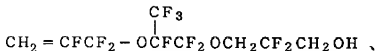
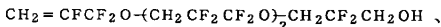
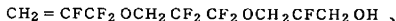
It comes out and is fluorine-containing olefin shown.

The desirable example of the fluorine-containing olefin shown by (2-a),



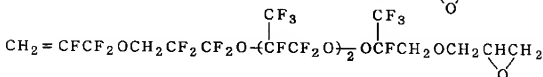
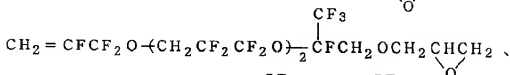
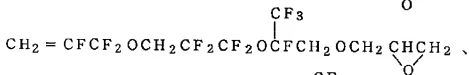
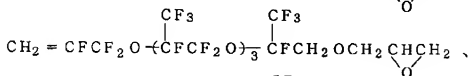
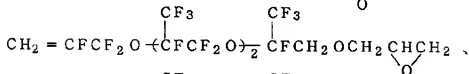
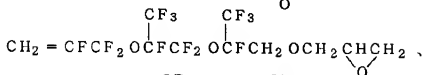
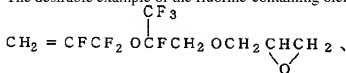
**** is raised.

The desirable example of the fluorine-containing olefin shown by a formula (2-b),
 $\text{CH}_2 = \text{CFCF}_2\text{OCH}_2\text{CF}_2\text{CH}_2\text{OH}$,



**** is raised.

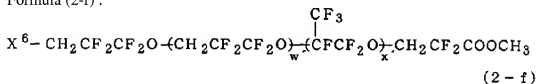
The desirable example of the fluorine-containing olefin shown by a formula (2-c),



Solvents are alcoholic solvent, such as water, methanol, and ethanol, and ether, Hydrocarbon system solvents, such as ether system solvents, such as tetrahydrofuran, mono-glyme, a jig lime, and dioxane, pentane, hexane, and cyclohexane, etc. are desirable, alcoholic solvent is desirable and ethanol is especially the most desirable. reaction temperature - it is still more desirable to make 20 degrees C - 80 degrees C of subproducts of the hydrogenation reaction of X5-CH2- (X5 is Br or I) by -10 degrees C - 20 degrees C, and a reducing agent or the reaction to CH2=CF-binding react in -5 degrees C - 10 degrees C also from the meaning reduced more preferably. The reaction which forms a double bond by deX5F (X5 is Br or I) of X5CH2CF2- can be attained the same with having used the above-mentioned Zn.

The glycidyl group content fluorine-containing olefin shown by a formula (2-c) is compoundable with the reaction of corresponding hydroxy group content fluorine-containing olefin of a formula (2-a) and epichlorohydrin. The method is compoundable by the method more nearly same than the compound of a formula (1-h) mentioned above with dealing in glycidyl group content fluorine-containing olefin of a formula (1-m). The hydroxy group content fluorine-containing olefin shown by a formula (2-b) can also be guided from the carboxylate which corresponds similarly.

Formula (2-f) :



[-- the inside of a formula, and X6 -- integer] of the integer of Br or I, w'0, or 1-5, x'0, or 1-10

That is, (2-b) is compoundable by the method more nearly same than the compound of a formula (2-e) with compounding fluorine-containing olefin of a formula (2-a) except using a formula (2-f).

Moreover, it is compoundable with the reaction of that the glycidyl group content fluorine-containing olefin shown by a formula (2-d) is also the same with dealing in (2-c) (2-b), and epichlorohydrin.

The 2nd is a general formula (V) which has carboxylic acid or a carboxylic acid derivative as a functional group of functional group content fluorine-containing olefin of this invention.

CH2=CFCF2-Rf8- (CH2)m-COOR4 (V)

As for the inside of [type, and R4, H, the alkyl group of carbon numbers 1-6, Na and K, Li or NH4, and Rf8 are the alkylene group or -ORf9 of carbon numbers 3-40 by which fluorine displacement was carried out. - (ether group by which fluorine displacement of the alkylene group by which fluorine displacement of the carbon numbers 2-40 was carried out Rf9, or the carbon numbers 3-50 was carried out) m is] which is the integer of 0, or 1-6.

It comes out and is fluorine-containing olefin shown.

In fluorine-containing olefin of a general formula (V), as for the structure of Rf8, one is the alkylene group by which fluorine displacement of the carbon numbers 3-40 was carried out, and the shape of a normal chain, branched state, or its mixture is also contained.

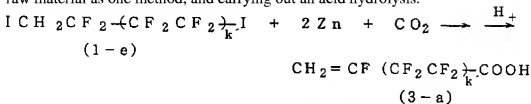
The example of representation desirable in it is a formula (3): $\text{CH}_2=\text{CFCF}_2\text{CF}_2\text{-(CF}_2\text{CF}_2\text{)}_{y'}\text{-(CH}_2\text{)}_{z'}\text{-COOR}_5$ (3)

[-- the inside of a formula, R_5 , and z' -- R_4 of said general formula (V), and m -- the same -- y' -- integer] to 1-10

It comes out and is fluorine-containing olefin shown.

The desirable example of the fluorine-containing olefin shown by a formula (3), $\text{CH}_2=\text{CFCF}_2\text{CF}_2\text{CF}_2\text{CF}_2\text{COOH}$, $\text{CH}_2=\text{CFCF}_2\text{CF}_2(\text{CF}_2\text{CF}_2)_2\text{-COOH}$, $\text{CH}_2=\text{CFCF}_2\text{CF}_2(\text{CF}_2\text{CF}_2)_3\text{-COOH}$, $\text{CH}_2=\text{CFCF}_2\text{CF}_2\text{CF}_2\text{CF}_2\text{CH}_2\text{COOH}$, $\text{CH}_2=\text{CFCF}_2\text{CF}_2\text{CF}_2\text{CF}_2\text{COOCH}_3$, $\text{CH}_2=\text{CFCF}_2\text{CF}_2(\text{CF}_2\text{CF}_2)_2\text{-COOCH}_3$, $\text{CH}_2=\text{CFCF}_2\text{CF}_2\text{CF}_2\text{CF}_2\text{COONa}$, $\text{CH}_2=\text{CFCF}_2\text{CF}_2(\text{CF}_2\text{CF}_2)_2\text{-COONa}$, $\text{CH}_2=\text{CFCF}_2\text{CF}_2\text{CF}_2\text{CF}_2\text{COONH}_4$, $\text{CH}_2=\text{CFCF}_2\text{CF}_2(\text{CF}_2\text{CF}_2)_2\text{-COONH}_4$, etc. are raised.

Although the synthetic method of the fluorine-containing olefin shown by a formula (3) can be variously chosen, for example when R is carboxyl group content olefin of H, It is the method of acquiring by making the above-mentioned poly fluoro alkyl iodide and carbon dioxide gas of (1-e) react under existence of zinc dust of 2Eq or more to (1-e) of a raw material as one method, and carrying out an acid hydrolysis.

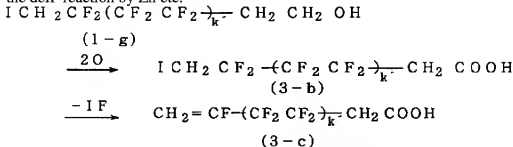


(ただし、 k は 2 以上の整数)

Carbon dioxide gas can be supplied in bubbling in ordinary temperature, or an autoclave, and under pressurization. As a solvent, dimethylformamide, dimethylacetamide, N-methyl pyrrolidone, dimethylsulfoxide, etc. are desirable, and dimethylformamide and dimethylacetamide are still more desirable. Reaction pressure is the range of 0 - 50 kgf/cm²G, and is 0 - 20 kgf/cm²G preferably.

0-150 degrees C of reaction temperature is 10-80 degrees C preferably.

As another method, it can pull to oxidation by the general oxidizing agent of the hydroxyl of the hydroxyl content compound of the above-mentioned formula (1-g), then can get by the delf reaction by Zn etc.



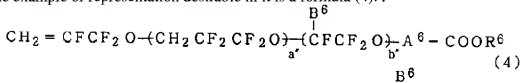
(ただし、 k は 2 以上の整数)

As an oxidizing agent ** and various things can use and For example, a Nichrome acid-sulfuric acid mixture, Manganese system oxidizing agents, such as a chromium system oxidizing agent called a chromium trioxide pyridine mixture, manganese dioxide, and

potassium permanganate, silver oxide, nitric acid, organic peroxide, etc. are desirable still more desirable, and a dichromic acid-sulfuric acid mixture is desirable, although reaction temperature changes with oxidizing agents to be used -- usually -20 degrees C -- 10-100-degree C 150 degrees C are -5-50 degrees C still more preferably preferably. it obtains -- having had (3-b) -- carboxyl group content fluorine-containing olefin (3-c) can be obtained with zinc like the above-mentioned method.

Set to fluorine-containing olefin of a general formula (V). Another structure of Rf8 is an ether group shown by -ORf9, Rf9 are the ether group by which fluorine displacement of the alkylene group by which fluorine displacement of the carbon numbers 2-40 was carried out, or the carbon numbers 3-50 was carried out, and the shape of a normal chain, branched state, or those mixtures are also contained.

The example of representation desirable in it is a formula (4) :

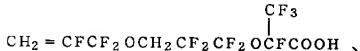
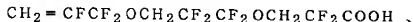
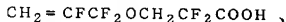
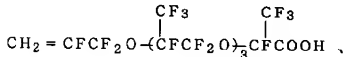
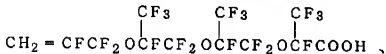
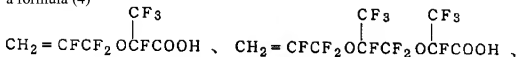


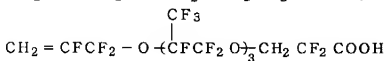
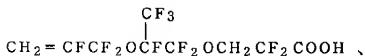
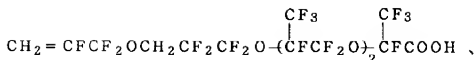
[式中、R⁶は一般式(V)のR⁴と同じ、A⁶は $\overset{\text{B}^6}{\underset{|}{\text{C}}}\text{F}$ -

Or the integer of 0, or 1-5 and b " (CF3 or F, and a ") of -CH2CF2- and B6 are the integers of 0, or 1-10, and, in the case of a"=b"=0, B6 is CF3].

It comes out and is fluorine-containing olefin shown.

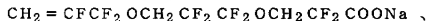
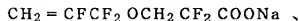
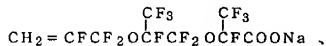
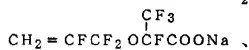
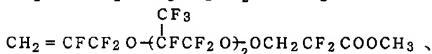
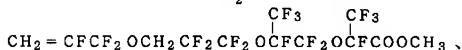
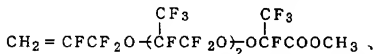
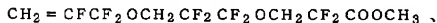
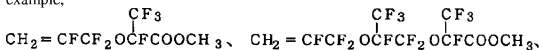
About carboxyl group content fluorine-containing olefin among the desirable examples of a formula (4)

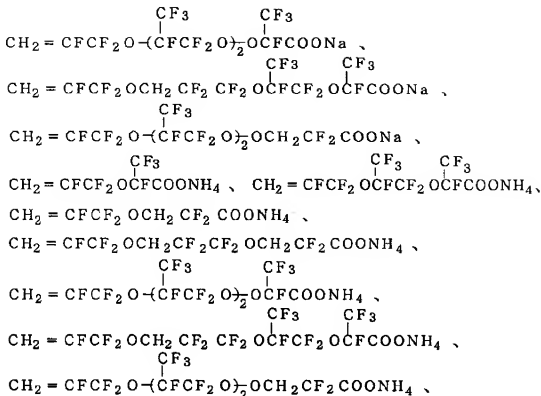




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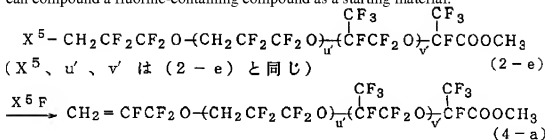
Said carboxylic acid derivative is alkyl ester, the sodium salt, the potassium salt, lithium salt, or ammonium salt equivalent to each of said carboxylic acid, and is the desirable example,





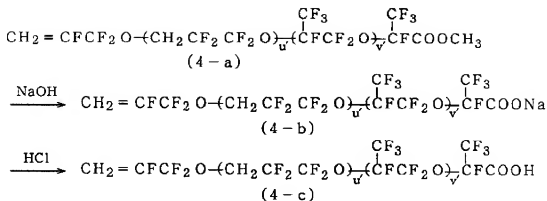
**** is raised.

although various synthetic processes of the carboxylic acid shown by a formula (4) and a carboxylic acid derivative are considered -- the above-mentioned formula (2-e) -- or (2-f) can compound a fluorine-containing compound as a starting material.



For example, when a formula (2-e) is used, it can deal in the fluorine-containing olefin (4-a) which has an ester group with the same zinc as the above-mentioned etc. by carrying out deXSF (X5:I or Br) reaction.

Carboxyl group content fluorine-containing olefin is obtained by hydrolyzing the ester group of the formula (4-a) obtained by the above-mentioned deIX5 (X5:I, Br).



Hydroxylation alkalis (MOH), such as sodium hydroxide, are made to react to fluorine-containing olefin, and that is, (4-a) is compoundable by making inorganic proton acid, such as hydrochloric acid and sulfuric acid, act, after a formula (4-b) generates.

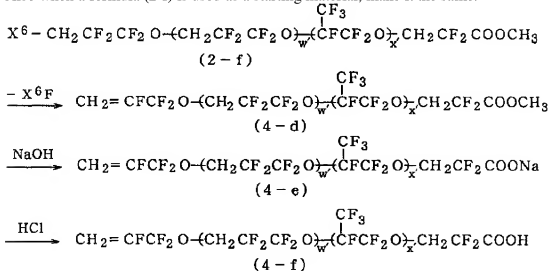
In said hydrolysis, it is obtained by acting inorganic proton acid, such as hydrochloric acid besides hydroxylation alkalis, such as sodium hydroxide, potassium hydroxide, and lithium hydroxide, sulfuric acid, and nitric acid.

In the case of alkali hydrolysis, although the solvent can use 1.0-1.1Eq of water or alcohols using a few excessive quantity to a compound (4-a), as for a hydroxylation alkali, it is desirable to use methanol or ethanol. 5-150 degrees C of reaction temperature are desirable, and its further 10-50 degrees C are desirable.

It can deal in carboxyl group content fluorine-containing olefin of (4-c) by adding inorganic proton acid (hydrochloric acid and sulfuric acid being desirable) until pH becomes two or less acidity in a solution [having been obtained (4-b)].

[the sodium salt, the potassium salt, lithium salt, or ammonium salt of carboxylic acid] Carboxyl group content fluorine-containing olefin [having been obtained above (4-c)] is neutralized by the general method using each aqueous solution of sodium hydroxide, potassium hydroxide, lithium hydroxide, or ammonia. It can get, respectively.

Also when a formula (2-f) is used as a starting material, make it the same.



It can deal in corresponding carboxyl ester group content fluorine-containing olefin (4-d)

carboxyl group content fluorine-containing olefin (4-f) and its alkali metal salt, and ammonium salt.

Fluorine-containing olefin of this invention The ethylene nature unsaturated compound of (1) versatility, Especially, in the case of copolymerization with fluorine-containing ethylene nature unsaturated compounds, such as tetrafluoroethylene and vinylidene fluoride, a rate of polymerization is not reduced remarkably and it has copolymeric [good], (2) Set to not reducing the thermal stability of the obtained fluorine-containing copolymer, and chemical stability, (3) fluorine-containing olefin itself, and alkaline conditions. It is stable, and the process for dealing in that it is not influenced by the operating condition but is easy to use and (4) fluorine-containing olefin is comparatively easy, and economical. It is the useful compound which can have the features it can carry out industrially and can introduce reactant machines, such as a hydroxy group, a carboxyl group, and a glycidyl group, into a fluorine-containing copolymer at a side chain.

Moreover, fluorine-containing olefin itself can consider the use as macromere. The fluorine-containing compound which generally has the structure of a carboxyl group or its alkali metal salt, and ammonium salt has high surface activity, and is useful as an emulsifier. Carboxyl group content fluorine-containing olefin of this invention or its Na and K, Li, and ammonium salt are formulas (5). : $\text{CH}_2=\text{CFCF}_2\text{Rf10}-(\text{CH}_2)_d-\text{COOR}^7$ (5)

[R⁷ is chosen from H, Na, K, and NH₄ among a formula, and d is the same as m of a formula (V).]

It was come out and expressed and Rf10 called it the fluorine-containing alkylene group of carbon numbers 3-40, or -ORf11- (Rf11 are the fluorine-containing alkylene group of carbon numbers 2-50, or the fluorine-containing ether group of carbon numbers 3-50) in the structure. The thing including a carbon number or an ether linkage is fluorine-containing olefin of the long chain which it had three or more, respectively in the sum total of the number of oxygen which participates in carbon and an ether linkage. As compared with the thing of 1 or 2, the sum total of a carbon number or a carbon number, and the number of oxygen that participates in an ether linkage has high surface activity, and can use as a reactant emulsifier.

By using this, in the case of emulsion polymerization, it contributes to diameter[of a granule]-izing of an emulsion, a raise in a yield, and improvement in a rate of reaction, and a soap free polymerization etc. is enabled.

Moreover, the contribution to the dispersion stability of the emulsion obtained by emulsion polymerization is also large, and since the amount used can be reduced not using a common free emulsifier, the use as a stable aqueous emulsion coating material the high weatherability of an emulsion itself and chemical-resistant is expectable.

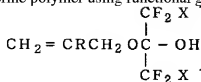
The 2nd is related with the functional group content fluorine polymer obtained by carrying out copolymerization of the ethylene nature unsaturated compound (B) to the fluorine-containing olefin (A) which has the hydroxy group of this invention, a glycidyl group, a carboxyl group, or a carboxylate machine.

The copolymer with a fluorine-containing ethylene nature unsaturated compound is reported variously, using the functional group monomer of a high draw carbon system first as conventional technology about a functional group content fluorine polymer.

For example, a copolymer with hydroxyalkyl vinyl ether and tetrafluoroethylene (USP3,306,879), Although there is a report of the copolymer (JP,H1-110646,A) using the

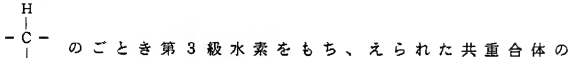
copolymer (JP,S59-52645,B) carboxyl group content vinyl ether compound using glycidyl vinyl ether etc., The fluorine polymer using the functional group monomer of these high draw carbon system runs short of the heat-resisting properties of both portion of a side chain, and portion of a principal chain, in particular, decomposition arises partially at the time of fusion kneading in high temperature with heat-resistant thermoplastics, and the thing of sufficient appearance and physical properties is not obtained.

What is known as a fluorine polymer using functional group content fluorine-containing



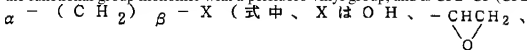
olefin on the other hand,

Although there is a fluorine polymer (JP,S50-143888,A) using (it is among a formula and H or methyl, and X' of R are F and Cl) and hemiacetal, these are in a polymer principal chain.



A heat-resisting property falls and it has the fault which is easy to carry out coloring deterioration at high temperature.

Moreover, it is considered as the fluorine polymer which carried out copolymerization of the functional group monomer with a perfluoro vinyl group, and is $\text{CF}_2=\text{CF}(\text{CF}_2)$.



- The fluorine polymer using the fluorine-containing monomer of being COOH (JP,S60-67517,A), Although there is a report of the fluorine polymer which carried out copolymerization of each fluorine-containing monomer of $\text{CF}_2=\text{CFO-R}'\text{-COOH}$ (JP,H3-234753,A) and $\text{CF}_2=\text{CFOR}'\text{-CH}_2\text{OH}$ (JP,H3-91513,A, the official announcement Taira No. 503935 [five] gazette) Polymerization reactivity with ethylene, tetrafluoroethylene, chlorotrifluoroethylene, etc. is low, in order to deal in the polymer which has a predetermined presentation, the monomer which has these perfluoro vinyl group needs a lot of preparations, and its fall of copolymerization velocity is also remarkable.

Furthermore, a complicated process is needed for synthesis, and these monomers are expensive and industrially lacking in practicality.

Moreover, the report which deals in a functional group content fluorine polymer by making a nucleophilic functional group add to the double bond which was made to carry out the defluoric acid of the vinylidene fluoride system polymer, and generated it (Polym.Mater.Sci Eng., 49,518 (1983)) Although there is also JP,H5-112616,A [the fluorine polymer obtained by these polymers reaction] It is hard to introduce a functional group uniformly, and in order to give producing presentation distribution and a functional group, it has faults, like that the heat-resisting property of the side chain portion of the

polymer generated when a nucleophilic reactant reagent added and chemical resistance are inadequate, and a polymer is further restricted to a vinylidene fluoride system polymer.

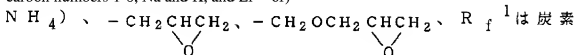
The purpose of this invention solves the above faults, and it offers the new fluorine polymer into which useful functional groups, such as a hydroxy group, a glycidyl group, and a carboxyl group, were introduced, without spoiling an outstanding heat-resisting property, chemical resistance, etc. which a fluororesin has in itself.

It is having the heat-resisting property which can be equal to fusion kneading in itself high temperature enough in detail in the case of the blend with heat-resistant thermoplastics, The thermoplastics and the fluorine polymer in the blend thing furthermore obtained keep good relations well mutually according to the effect of a functional group, and the functional group content fluorine polymer characterized by the ability to form a uniform distributed state is offered.

this invention -- the following -- it is the copolymer obtained by carrying out copolymerization of (A) and the (B) -- (A) -- 0.01 - 80mol %, and (B) -- 20 - 99.99mol % -- it contains and is related with the new functional group content fluorine polymer characterized by number average molecular weights being 2000-20,000,000.

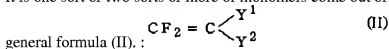
(A) is a general formula (I). : $\text{CH}_2=\text{CFCF}_2\text{-Rf}_1\text{-(CH}_2\text{)}_a\text{-X}_1$ (I)

the inside of [type, and X_1 - CH_2OH and - COOR_1 (here -- R_1 -- H, the alkyl group of carbon numbers 1-6, Na and K, and Li -- or)

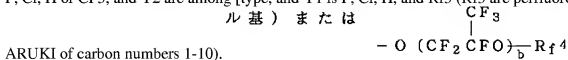


the alkylene group by which fluorine displacement of several 1-40 was carried out or - ORf_2 - (ether group by which fluorine displacement of the alkylene group by which fluorine displacement of the carbon numbers 1-40 was carried out Rf_2 , or the carbon numbers 3-50 was carried out), and a are the integers of 0, or 1-6 --]

It is one sort or two sorts or more of monomers come out of and shown, and (B) is a

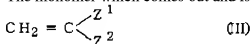


F, Cl, H or CF_3 , and Y_2 are among [type, and Y_1 is F, Cl, H, and Rf_3 (Rf_3 are perfluoro
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(Rf_4 are the perfluoroalkyl machine of carbon numbers 1-6, and b is the integer of 0, or 1-5)

The monomer which comes out and is shown by existing], and general formula (III) :



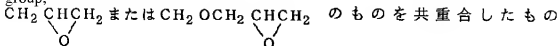
The inside of [type and Z_1 are the alkyl groups of F, H, and carbon numbers 1-6. Or the perfluoroalkyl machine of carbon numbers 1-10 and Z_2 are one sort or two sorts or more of monomers chosen from the group which consists of a monomer shown by the alkyl

group of H, Cl, and carbon numbers 1-6, or $-(CF_2)_d-Z_3$ (d is integer of 1-10 and Z_3 is F or H).

That is, the polymer of this invention is the formula (I) containing one functional group of a hydroxy group, a carboxyl group, a carboxylic acid derivative, a glycidyl group, and a glycidyl ether machine.

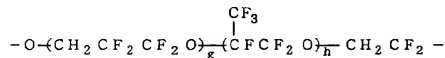
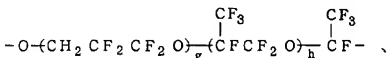
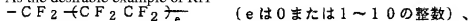
It is the new functional group content fluorine polymer obtained by being alike and carrying out copolymerization of fluorine-containing olefin (A) 0.01 of the specific structure shown - the 80mol % to an ethylene nature unsaturated compound (B).

Although functional group content fluorine-containing olefin (A) is shown in a formula (I) in the fluorine polymer of this invention, X_1 is $-CH_2OH$ and $-COOH$ as a functional group.



** -- it is desirable. Moreover, Rf_1 in a compound (A) is a fluorine-containing oxyalkylene machine shown by a fluorine-containing alkylene group or $-ORf_2$, and Rf_2 are a fluorine-containing alkylene group or a fluorine-containing ether group further. When thinking especially a heat-resisting property as important, Rf_1 has that desirable by which fluorine displacement was carried out more highly, and the perfluoro-ized alkylene group or its an oxyalkylene machine is desirable. Moreover, although the chain length of Rf_1 can choose the thing of about one to 40 carbon number by a use, what has about two to 20 carbon number from the field of copolymeric and the physical properties of a copolymer is desirable.

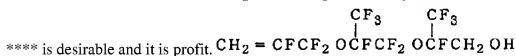
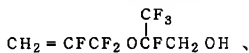
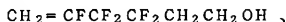
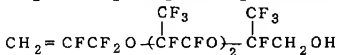
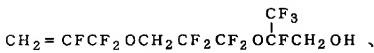
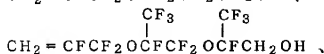
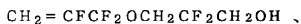
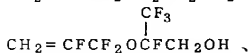
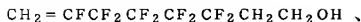
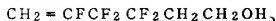
As the desirable example of Rf_1



(g は 0 または 1 ~ 5 の整数、 h は 0 または 1 ~ 10 の整数)

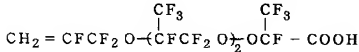
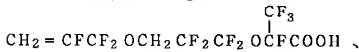
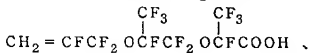
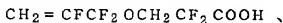
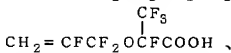
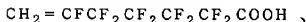
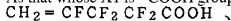
*** is illustrated.

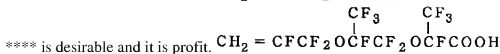
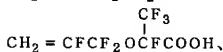
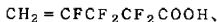
As that whose X_1 is furthermore $-CH_2OH$ as an example of the compound of (A)



** -- it is desirable.

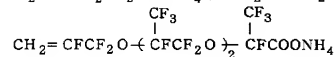
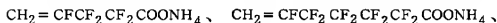
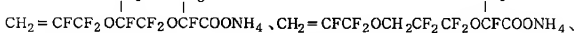
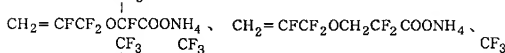
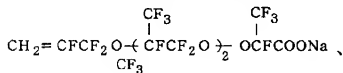
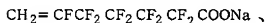
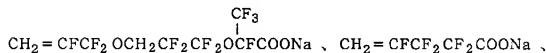
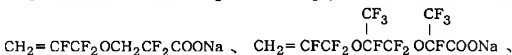
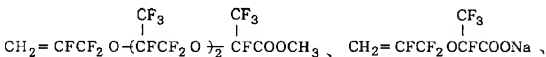
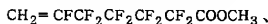
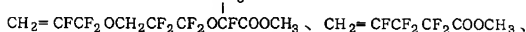
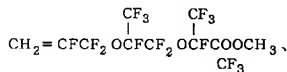
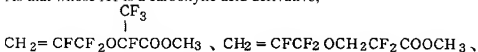
As that whose XI is - COOH group





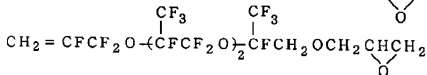
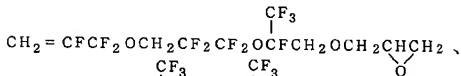
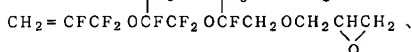
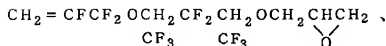
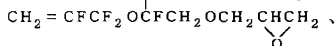
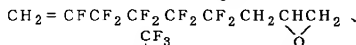
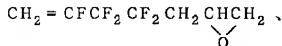
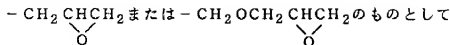
** -- it is desirable.

As that whose X1 is a carboxylic acid derivative,

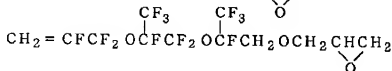
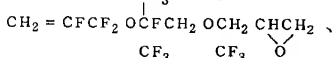
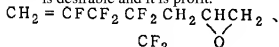


**** is desirable.

X¹が

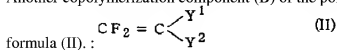


**** is desirable and it is profit.



** -- it is desirable.

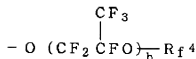
Another copolymerization component (B) of the polymer of this invention is a general



formula (II). :

F, Cl, H or CF₃, and Y₂ are among [type, and Y₁ is F, Cl, H, and Rf₃ (Rf₃ are perfluoro

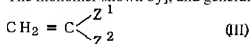
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ARUKI of carbon numbers 1-10).

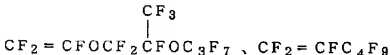
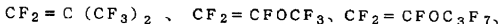
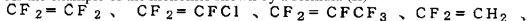
(Rf₄ are the perfluoroalkyl machine of carbon numbers 1-6, and b is the integer of 0, or 1-5)

The monomer shown by], and general formula (III):



[-- the formula (II) in which Z¹ is shown by the alkyl group of F, H, and carbon numbers 1-6, or the perfluoroalkyl machine of carbon numbers 1-10 among a formula, and Z² is shown by the alkyl group of H, Cl, and carbon numbers 1-6, or -(CF₂) d-Z₃(d is integer of 1-10 and Z₃ is F or H)] And they are one sort or two sorts or more of monomers chosen from the group which consists of a formula (III).

As the example of the monomer shown by a formula (II)



**** is raised preferably.

As the example of the monomer shown by a formula (III) ** CH₂=CHF CH₂=CFCF₃, CH₂=CHCF₃, CH₂=C(CF₃)₂, CH₂=CH₂, CH₂=CHCH₃, CH₂=CHC₂H₅, CH₂=C(CH₃)₂, and CH₂=CHCl, CH₂=CHC₄F₉, CH₂=CF(CF₂)₃-H, etc. can raise preferably.

Although the molar ratio of the monomer (B) of functional group content fluorine-containing olefin in the fluorine polymer of this invention (A) and others may change with kinds of a use or copolymer, they are usually (A)/(B)=0.01 - 80/20 - 99.99mol %. It is (A)/(B) in order to deal in the good constituent of dispersibility especially in the case of the blend with heat-resistant thermoplastics.

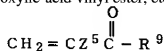
= 0.01 - 30 / 70-99.99mol% of presentation is desirable.

Copolymerization of the ethylene nature unsaturated compound (C) in which the fluorine-containing copolymer of this invention is still as copolymerizable as a compound (A) and (B) other than the aforementioned compound (A) and (B) may be carried out.

As said ethylene nature unsaturated compound **, for example, formula: CH₂=CH-O-(C=O) e" R₈ (the inside of a formula, and R₈ -- the aliphatic series machine of carbon numbers 1-17 --) The alicyclic machine of carbon numbers 3-17, the fluoro alkyl group of carbon numbers 1-20, e " -- 0 or 1 -- it is -- [alkyl vinyl ether or vinyl ester shown is raised, and] as an example For example, methyl vinyl ether, ethyl vinyl ether, n-propyl vinyl ether, Isopropyl vinyl ether, n-butyl vinyl ether, isobutyl vinyl ether, Cyclohexyl vinyl ether, 2 and 2, 2-trifluoroethyl vinyl ether, 2, 2, 3, and 3-tetrafluoro propyl vinyl ether, 2, 2, 3 and 3, 3-pentafluoro propyl vinyl ether, Acetic acid vinyl ester, propionic acid vinyl ester, butanoic acid vinyl ester, pivalate vinyl ester, BASA tic acid vinyl ester,

cyclohexane-carboxylic-acid vinyl ester, etc. are raised.

さらに式：



(H, Cl, F, CH₃, CF₃, and R₉ are among a formula, and Z⁵ is H, Cl, and F.) It is raised by the compound expressed with the aliphatic series machine of carbon numbers 1-17, the alicyclic machine of carbon numbers 3-17, or the fluoro alkyl group of carbon numbers 1-20, and as an example Isobutyl acrylate, methyl acrylate, ethyl methacrylate, 2, 2, 3, 3, and 3-pentafluoro propyl alpha-fluoro acrylate, 2, 2, 3, 3, 4, 4, 5, 5, 6, 6, 7, and 7-dodeca fluoro pentyl alpha-trifluoromethyl acrylate, Cyclohexyl acrylate, 2, 2, 3, 3, 4, 4, 5, 5, 6, 6, 7, 7, 8, 8, 9, 9, 10, 10, 11, 11, 12, 12, 13, 13, 14, 14, 15 and 15, and 15-nonacosu fluoro pentadecyl acrylate, Octyl alpha-chloro acrylate, octadecyl acrylate, etc. are raised.

Moreover, the compound shown by formula:CH₂CHCH₂Z₆ (Z₆ shows the alkoxy group of a chlorine atom or carbon numbers 1-8 among a formula) can also be used, and it is an example. A **** allyl chloride, allyl compound methyl ether, allyl compound isopropyl ether, allyl compound octyl ether, etc. are raised all of a sudden.

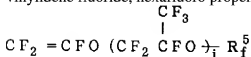
Moreover, in addition to this, styrene and a styrene derivative, and maleic acid dialkyl ester are raised.

Although the molar ratio of each monomer in a polymer in case copolymerization of the ethylene nature unsaturated compound (C) is carried out changes with kinds of a use or copolymer, they are usually (A)/(B) + (C) = 0.01 - 80/20 - 99.99mol %. It is desirable that a compound (C) is less than 60 mol % to the sum total mole of (B) and (C) about (B) and (C). In the case of the fluorine polymer used especially on the occasion of the blend with heat-resistant thermoplastics Since the portion of a compound (C) can turn into an unstable portion thermally, it is desirable that (A) is 0.01 - 30mol %, and 70 - 99.99mol %, and (C) is less than 20 mol % to the number of moles of all the monomers.

In the fluorine polymer of this invention, the performance and the physical properties of the polymer, and the use according to it are greatly influenced by the kind of compound (B), and presentation (ratio).

The desirable structure of the fluorine polymer in this invention can be divided roughly into two, what makes tetrafluoroethylene or chlorotrifluoroethylene a principal component, and the thing which makes vinylidene fluoride a principal component, in the kind of compound (B). namely, the 1st group -- as functional group content fluorine-containing olefin (A) and (B) Tetrafluoroethylene or chlorotrifluoroethylene is used as an essential ingredient. Are the fluorine polymer furthermore obtained by carrying out copolymerization of other copolymerizable monomers if needed, and (A) to the number of moles of all the monomers 0.01 - 30mol %, as opposed to the monomer sum total mole except fluorine-containing olefin (A) -- tetrafluoroethylene or chlorotrifluoroethylene -- more than 30 mol % -- it is the fluorine polymer to contain.

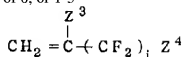
As a monomer with others copolymerizable in the aforementioned polymer, they are vinylidene fluoride, hexafluoro propene, hexafluoro isobutene, and a formula.:



(-- par full OROBI R_f⁵ are shown by perfluoroalkyl of carbon numbers 1-6 among a

formula, and j is indicated to be by integer) of 0, or 1-5

ニルエーテル類および式：



(-- H or F, and Z⁴ have [Z³] among a formula fluorine-containing olefin and ethylene and propylene in which H or F, and i are shown by integer) of 1-10, 1-butene, desirable isobutene, etc.

As the still more detailed example of the fluorine polymer of this invention which makes tetrafluoroethylene or chlorotrifluoroethylene a principal component Fluorine-containing olefin (A) and the copolymer of tetrafluoroethylene (what is called functional group content PTFE), The copolymer of a compound (A), tetrafluoroethylene, and hexafluoro propene (functional group content FEP), The copolymer which carried out copolymerization of the perfluoro vinyl ether shown above by less than 10 mol % to a compound (A), tetrafluoroethylene, and all the monomers except (A) (functional group content PFA), The copolymer which polymerized considering copolymerizable fluorine-containing olefin as the 3rd component monomer if needed in a compound (A), tetrafluoroethylene or chlorotrifluoroethylene, and an ethylene pan (functional group content E (C) TFE), Furthermore, the copolymer of the shape of an elastomer which carried out copolymerization of a compound (A), tetrafluoroethylene, and the propylene, The copolymer of the shape of an elastomer which carried out copolymerization of the perfluoro vinyl ether to the compound (A) at more than 15 mol % to tetrafluoroethylene and all the monomers except (A) etc. is raised preferably.

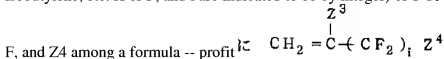
Although it changes with kinds of heat-resistant thermoplastics when using it especially for the blend with heat-resistant thermoplastics, The working temperature of heat-resistant thermoplastics and the comparatively alike working temperature can be chosen in the case of a fusion blend or shaping. The thermal stability in the temperature is maintained, and a fluorine polymer is desirable, and in the aforementioned illustration Similarly especially a copolymer aforementioned PFA type [containing a compound (A)], and an E(C) TFE type copolymer and the copolymer of the shape of an elastomer which made the principal component the aforementioned tetrafluoroethylene containing (A) are desirable.

Receive the number of moles of all the monomers for details with the PFA type copolymer in it. the mol of the monomer excluding [functional group content fluorine-containing olefin (A)] 0.01 - 30mol % and a compound (A) -- as opposed to the total quantity of a number -- tetrafluoroethylene 95 - 99.7mol %, and formula:CF₂=CFORf12 (among a formula) Rf12 are 0.3-5.0mol of perfluoro vinyl ether% of copolymer shown with the perfluoroalkyl machine of carbon numbers 1-6.

moreover, an E(C) TFE type copolymer -- detailed Functional group content fluorine-containing olefin (A) to the number of moles of all the monomers 0.01 - 30mol %, They are the fluorine-containing olefin 0 of the 3rd component used tetrafluoroethylene 30 - 70mol % and ethylene 30 - if needed [70mol / % and if needed] to the monomer sum total except a compound (A) - 15mol% of a copolymer. As the fluorine-containing olefin

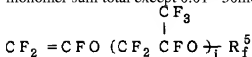
as the 3rd component,
$$\text{CH}_2 = \overset{\text{Z}^3}{\underset{|}{\text{C}}} - (\text{CF}_2)_i \text{Z}^4$$

(-- fluorine-containing olefin, perfluoro vinyl ether, hexafluoropropylene, hexafluoro isobutylene, etc. H or F, and i are indicated to be by integer) of 1-10 can use Z3 for H or



The hexafluoro isobutylene as the above with (same) Z3, Z4, and i etc. is desirable. The copolymer of the shape of an elastomer which, on the other hand, makes tetrafluoroethylene containing a functional group a principal component, one -- functional group content fluorine-containing olefin (A) -- the mol of all the monomers -- the mol of the monomer excluding 0.01 - 30mol % and a compound (A) to the sum total of a number -- it is the copolymer which tetrafluoroethylene becomes from 40 - 70mol % and propylene 30 - 60mol % to the sum total of a number, moreover -- these -- others -- the mol of the monomer excluding (A) in hexafluoropropylene, copolymerizable component, for example, vinylidene fluoride, chlorotrifluoroethylene, and perfluoro vinyl ether -- as opposed to the sum total of a number -- less than 20 mol % -- it can also contain.

Another elastomer-like polymer is a polymer which consists of tetrafluoroethylene and perfluoro vinyl ether, and the sum total of the number of moles of all the monomers is received, Compounds (A) are tetrafluoroethylene 40 - 85mol % and a type to the monomer sum total except 0.01 - 30mol %, and (A). :



(-- Rf5 are shown by the perfluoroalkyl machine of carbon numbers 1-6 among a formula, j is shown by integer) of 0, or 1-5, and they are perfluoro vinyl ether 15 - 60mol% of a polymer.

In this invention, the 2nd group of a desirable fluorine polymer is a polymer which makes vinylidene fluoride a principal component.

That is, use vinylidene fluoride as an essential ingredient as functional group content fluorine-containing olefin (A) and (B), and carry out copolymerization of other monomers if needed further. it is the copolymer obtained -- the mol of all the monomers - the mol of the monomer excluding [the compound (A)] 0.01 - 30mol %, and (A) to the number -- as opposed to the sum total of a number -- vinylidene fluoride -- more than 40 mol % -- it is the fluorine polymer to contain.

In said polymer, tetrafluoroethylene, chlorotrifluoroethylene, hexafluoro propene, hexafluoro isobutene, and perfluoro vinyl ether are desirable examples as other copolymerizable monomers.

As the example of the fluorine polymer of this invention which makes vinylidene fluoride a principal component, The copolymer (what is called functional group content PVdF) of functional group content fluorine-containing olefin (A) and vinylidene fluoride, a compound (A), and vinylidene fluoride, A copolymer with tetrafluoroethylene, the copolymer of a compound (A), vinylidene fluoride, and hexafluoropropylene, A copolymer with the copolymer of a compound (A), vinylidene fluoride,

tetrafluoroethylene, and hexafluoropropylene, a compound (A), vinylidene fluoride and tetrafluoroethylene, and chlorotrifluoroethylene etc. is raised preferably.

These fluorine polymers that make vinylidene fluoride a principal component can be made into the polymer of the shape of resin, or the shape of an elastomer in more detail by choosing various other existence, kinds, and composition ratios of a monomer component which carry out copolymerization.

The blend with heat-resistant thermoplastics is faced in it, and it is an example of the polymer of the shape of especially desirable resin, One Functional group content fluorine-containing olefin (A) 0.01 - 30mol %, 70-99mol of vinylidene fluoride% of copolymer and, and a compound (A) to the number of moles of all the monomers 0.01 - 30mol %, Vinylidene fluoride to the sum total of the number of moles of the monomer except a compound (A) And 70 - 99mol %, As opposed to the sum total of the number of moles of the monomer tetrafluoroethylene receives 1-30mol% of a copolymer, and a compound (A) receives the number of moles of all the monomers, and excluding 0.01 - 30mol % and a compound (A) 50-99mol of vinylidene fluoride % and 0-30mol of tetrafluoroethylene %, As opposed to the sum total of the number of moles of the monomer excluding [1-20mol of chloro trifluoro ERECHIN% of copolymer, and a compound (A)] 0.01 - 30mol % and the compound (A) of all the monomers 60-99mol of fluorination BINIRITEN % and 0-30mol of tetrafluoroethylene % and 1-10mol of hexafluoropropylene% of copolymer etc. is raised.

Moreover, a compound (A) should receive the number of moles of all the monomers as an example of the presentation range which becomes elastomer-like. the mol of the monomer except 0.01-30mol % and a compound (A) -- to the sum total of a number, tetrafluoroethylene 0 - 30mol % are raised for vinylidene fluoride, and 10 - 50mol% of a copolymer are preferably raised for hexafluoropropylene 40 - 90mol%.

Copolymerization of the functional group content fluorine-containing olefin (A) is carried out in the case of manufacture of fluorine-containing segmentation polymer which is furthermore indicated to JP,S61-49327,B in the example of the fluorine polymer of this invention. The functional group content fluorine-containing segmentation polymer obtained is also contained.

That is, the iodine atom isolated from the iodide compound which has fundamentally the iodine atom combined with the carbon atom with fluorine-containing segmentation polymer, it intervenes from this iodide compound between the residue except this iodine atom, and this iodine atom and this residue -- if small, let two sorts of polymer chain segments (however, at least one sort of them is a fluorine-containing polymer chain segment) be indispensable composition components It becomes. If it puts in another way, fluorine-containing segmentation polymers of this invention will be at least two sorts of polymer chain segments (however, at least one sort of them is a fluorine-containing polymer chain segment) fundamentally.

** and others -- it becomes considering the residue excluding this iodine atom from the iodine atom isolated from the iodide compound which has the iodine atom combined with the chain and the carbon atom which exists in the both ends, and this iodide compound as a part for indispensable composition. namely, :Q-[(A-B-) I]f which can express the typical structure of the fluorine-containing segmentation polymer of this invention with the following formula -- the inside of [type, and Q -- an iodide compound to an iodine atom f " is the iodine atom with which a polymer chain segment (however, at least one of

them is a fluorine-containing polymer chain segment) and I were isolated from said iodide compound by the removed residue, A, B, and, respectively, and] showing the number of the joint hands of Q.

About the functional group content fluorine-containing segmentation polymer which carried out copolymerization of the functional group content fluorine-containing olefin (A) of this invention It is the fluorine-containing copolymer which introduced functional group content fluorine-containing olefin (A) into one of segments, or both segments (two or more sorts of segments) according to copolymerization among two sorts (or three sorts) of segments in the polymer.

The molecular weight of the fluorine polymer of this invention is, for example at a shaping use, although suitable ranges especially differ and it is not limited by the kind of polymer, a use, and directions for use. Generally, it is the fluorine polymer itself or especially more than [about 5000] are [2000 or more] usually preferably desirable [that it is not much low from a point of the mechanical hardness of the blend thing] in the case of the blend with heat-resistant thermoplastics as a number average molecular weight. Moreover, especially less than [about 750000] is [1 million or less] usually preferably desirable [that it is not much high] from a point of moldability.

Make the aforementioned tetrafluoroethylene into a principal component in the example of the fluorine polymer of this invention in more detail. When it is each containing a resin-like copolymer (A), for example, functional group content fluorine-containing olefin, PFA, FEP, and the fluorine polymer in which fusion processing like an ETFE type polymer is possible, the melt flow value is the kind of fluoro resin, respectively.

***** measurement temperature (for example, [a PFA and FEP type polymer] 372 degrees C) setting an ETFE type polymer against 300 degrees C and load (for example, 7kg) -- 0.01×10^{-2} - 50×10^{-2} ml/sec. -- desirable -- 0.05×10^{-2} - 25×10^{-2} ml/sec. -- it is 0.1×10^{-2} - 10×10^{-2} ml/sec. especially preferably.

Moreover, a compound (A) is included in the aforementioned example of the polymer of this invention. A polymer, the polymer of a compound (A) and vinylidene fluoride, and (A) and vinylidene fluoride of the shape of an elastomer which makes tetrafluoroethylene a principal component, In the case of a fluorine polymer meltable to solvents, such as DMF which furthermore consists of one or more sorts of tetrafluoroethylene, hexafluoroethylene, and chlorotrifluoroethylene, such as a polymer of the shape of resin, or the shape of an elastomer, and THF, for example, the determination-of-molecular-weight value of the polystyrene conversion by GPC -- a number average molecular weight -- 2000-1 million -- desirable -- 5000-750000 -- it is the thing of 10000-500000 especially preferably It is.

Moreover, the amount object of polymers of a compound (A) and tetrafluoroethylene which cannot carry out fusion processing again other than them with a with a molecular weight of about 2000 to 1 million currently called the common-name low molecular weight PTFE from the oligomer-like thing thing in the case of a copolymer Although an implication and the molecular weight in that case cannot be specified, they are 1 million-10 million, and about a maximum of 20 million about.

The fluorine polymer of this invention can be manufactured according to any polymerization form, such as suspension polymerization, emulsion polymerization, solution polymerization, and block polymerization, and can mainly choose a polymerization method suitably by the kind and use of a polymer.

The oil-soluble radical polymerization initiator used when manufacturing the copolymer of this invention by suspension polymerization. Generally it is used and is easy to be organic peroxide; types, such as diisopropyl peroxy dicarbonate, di-n-propyl peroxy

dicarbonate, and isobutyl peroxide. :
$$[Y^3 \leftarrow C F_2 \rightarrow \overset{\overset{O}{||}}{C} O]_2$$

The inside of [type and Y3 are a hydrogen atom and a fluorine atom. Or the peroxide shown by integer] of 2-8 is raised, and, specifically, a chlorine atom and g " of JIPA fluoro PUROPIONIRU peroxide, JI (omega-hydronalium perfluoro hexa noil) peroxide, JI (omega-chloro perfluoro pro PIONIRU) peroxide, etc. can be illustrated. Moreover,

formula :
$$[C 1 \leftarrow (C F_2 \leftarrow C F C 1)_h \leftarrow C F_2 \leftarrow \overset{\overset{O}{||}}{C} O]_2$$

[-- h " of azo compounds, such as fluorine system organic peroxide, such as the peroxide shown by integer] of 1-10, for example, JI (TORIKURORO perfluoro hexa noil) peroxide etc., and azobisisobutyronitril, etc. are raised among a formula.

Although water and chloro fluoroalkanes are raised as a polymerization solvent, for example, the mixed solvent of water and chloro fluoroalkanes is desirable, and it is desirable especially from the field of suspension dispersibility and economical efficiency that chloro fluoroalkane considers it as 10 to 100 weight % to water.

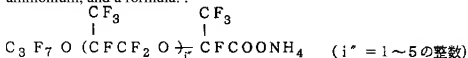
It is desirable to use a with a carbon number of about one to four thing especially as chloro fluoroalkanes. Specifically, they are dichlorodifluoromethane and dichloro monofluoromethane, Fluoro methane, such as monochlorodifluoromethane, monochlorotrifluoromethane, and tetrafluoromethane, Fluoro butane, such as fluoro propane, such as fluoro ethane, such as tetrafluoro ethane, trichlorofluoroethane, dichloro tetrafluoro ethane, and hexafluoro ethane, and dichloropentafluoropropane, and perfluoro cyclobutane, is illustrated. Dichloro tetrafluoro ethane, bird KUROROTORU fluoro ethane, dichloropentafluoropropane, and perfluoro cyclobutane are used preferably especially.

Moreover, necessity is accepted and it is the sake of molecular weight regulation. As a chain transfer agent, isopentane, n-hexane, cyclohexane, Methanol, ethanol, tert-butanol, carbon tetrachloride, chloroform, a methylene chloride, methyl chloride, fluorocarbon iodide (for example, CF₂I₂, CF₃I, I-(CF₂)₄-I, 2(CF₃)CFL, etc.), etc. can be used.

As the initiator used when manufacturing the polymer of this invention according to emulsion polymerization, Although the usual radical initiator can be used A water-soluble initiator is adopted preferably and specifically Persulfuric acid, such as an ammonium persulfate salt, The redox initiator which consists of combination with reducing agents, such as hydrogen peroxide or these and sodium hydrogensulfite, and sodium thiosulfate, Furthermore, dibasic acid peroxide, such as an inorganic system initiator of the system which made a small amount of iron, a ferrous salt, silver sulfate, etc. live together or disuccinic acid peroxide, and Digul tar acid peroxide, azobis isobutyl amidine dihydrochloride, etc. are raised to these. Moreover, the aforementioned oil-soluble initiator can be used similarly.

As an emulsifier, a FURUO carbon system emulsifier is adopted preferably, and,

specifically, they are perfluoro octanoic acid ammonium, perfluoro nonoic acid ammonium, and a formula. :



It comes the whole ** and the emulsifier of a fluorine-containing ether system etc. is raised preferably. Moreover, the surface active agent of the anion system of a high draw carbon system, a cation system, the Nonion system, and a betaine system can also be used if needed.

Furthermore, the same chain transfer agent and same buffer for pH as the above, a pH adjuster, etc. can also be used if needed.

When manufacturing the polymer of **** this invention to solution polymerization, it is a polymerization solvent. Acetone besides the aforementioned chloro fluoroalkanes, methyl ethyl ketone, Ester, such as ketone, such as methyl isobutyl ketone, ethyl acetate, and butyl acetate, Glycol ether, such as alcohols, such as aromatic hydrocarbon, such as toluene and xylene, methanol, ethanol, and isopropanol, ethylcellosolve, mono-glyme, and a jig lime, can be used.

The same thing as suspension polymerization can be used for a polymerization initiator, a chain transfer agent, etc.

the polymerization reaction conditions of the polymer of this invention are suitably chosen by the kind presentation of a polymer, reaction form, a polymerization initiator, a reaction medium, etc. -- usually -- reaction temperature -20 degree-C-150 degree C -- desirable -- 5-100 degrees C and polymerization pressure power -- 100kgf/cm2 -- it is less than 50 kgf/cm2G preferably G or less.

Moreover, in manufacture of the polymer of this invention, it is the method to the polymerization tank about each component (especially each component of a monomer, an initiator, and a chain transfer agent) to teach, You may carry out by the method which restriction in particular does not have and teaches the whole quantity of the various components used from the beginning of a polymerization, or the method of teaching a part or all of a component to a successive polymerization tub continuously or in fractionation.

The fluorine polymer of this invention can be used effective in the part demanded [solvent resistance / a heat-resisting property, chemical resistance, weatherability, oil resistance,] as a common molding material, a coating material, rubber adhesives, an ion exchange membrane, a sealant, etc. also besides being blended with heat-resistant thermoplastics.

The following use can be concretely performed especially using the functional group of the polymer of this invention.

What has a hydroxy group or a carboxyl group among functional group content fluorine-containing monomers (A) ** What is called PTFE, [the denaturation PTFE acquired by introducing into fluororesins, such as FEP, PFA, and ETFE, Denaturation FEP, Denaturation PFA, and Denaturation ETFE] It can deal in the moldings with which a bridge can be made to construct without addition of a cross linking agent, and beyond a

fusing point does not flow at the rate of high elasticity by performing heat treatment at the temperature of 200 degrees C or more for 1 hour or more, respectively. The quantity of the hydroxy group in the fluorine polymer in this case or carboxy group content fluorine-containing olefin is 0.1-20mol %. If there is too little functional group concentration, bridge formation will not be performed enough, but it becomes difficult to deal in the rate of high elasticity, without using a cross linking agent. On the other hand, if too large, the fusing point of a fluorine polymer will fall, and since it becomes difficult to maintain form in heat-treatment, precision shaping becomes difficult. It becomes easy to produce the internal distortion at the time of heat treatment, and becomes easy to generate a crack. Moreover, since the fault of a fluorine-containing copolymer becoming elastomer-like and moldability falling arises, it is not desirable. It is desirable that a hydroxy group or carboxyl group content fluorine-containing olefin is especially included at 0.2-10mol% of a rate.

** About fluorine-containing olefin (A), they are tetrafluoroethylene or

chlorotrifluoroethylene, and a formula. :
$$\text{CH}_2 = \text{CH} - \text{O} \left(\overset{\text{O}}{\underset{\text{||}}{\text{C}}} \right)_j \text{R}^{10}$$

the inside of a formula, and R10 -- the aliphatic series machine of carbon numbers 1-17, and the alicyclic machine of carbon numbers 3-17 -- The fluorine polymer obtained by introducing the fluoro alkylene group of carbon numbers 1-20, and j " into a copolymer with the alkyl vinyl ether shown by 0 or 1, or alkyl vinyl ester, Or the polymer of a vinylidene fluoride system containing a functional group as shown by Claim 14 or Claim 18 can serve as weatherability, chemical-resistant, and contamination-resistant outstanding paint resin.

When these fluorine-containing resin is used as a coating material, as an effect of a functional group, the functional group of i this invention and the curing agent in which a reaction is possible can be blended, and crosslinking reaction can be carried out with ordinary temperature or heating. That is, it is useful especially to use as ordinary temperature or a heating hardening type coating material, and the paint film excellent in weatherability, solvent resistance, and resistance to contamination can be formed. the content of the functional group in the case of using as a hardening machine -- 1-30mol % -- it is 3-20mol % preferably.

Multivalent isocyanates, a melamine curing agent, a urea resin curing agent, a polybasic acid curing agent, an epoxy curing agent, a multivalent amine curing agent, a polyamide curing agent, etc. can usually choose a curing agent suitably according to the functional group in a polymer.

ii) By raising the compatibility (pigment dispersibility) of the fluorine polymer at the time of making it the coating material containing a pigment, and a pigment, it is smooth and a little introduction of fluorine-containing olefin which has a carboxyl group in a compound (A) can obtain high gloss and the paint film which was excellent in weatherability. The required quantity of the carboxyl group content monomer in this case is 0.1-5mol %, and less than 3 mol % is especially enough as it.

iii) When it is considered as an aqueous emulsion coating material or water soluble paint, the introduction of the carboxyl group content monomer of this invention can give the dispersion stability and water solubility over water to a fluorine polymer.

the soluble grant to water [improvement / in a dispersion stability / to the water of an aqueous emulsion coating material] aiming at 0.1-10mol % and water soluble paint -- 5-30mol% of each -- it becomes possible by introduction of a carboxyl group content monomer.

iv) In addition to this, there are effects, such as the adhesion of the paint film to base materials, such as a metal, wood, concrete, and plastics, and improvement in the solvent solubility of a polymer and compatibility with a curing agent, by introduction of the functional group of this invention.

** The fluorine polymer of the shape of an elastomer containing a functional group as shown by Claim 17 or Claim 19 of this invention can serve as outstanding fluororubber of a heat-resisting property, chemical resistance, oil resistance, friction-proof and abrasiveness, and cold resistance.

i) When using as fluororubber, as an effect of functional group introduction By using the functional group of this invention as a bridge formation site, vulcanization can be advanced comparatively easily in a short time, and it can deal by it in a physical property, for example, the bridge formation product which pulled and was excellent in hardness, elongation, the heat-resisting property, the compression set, etc.

As a vulcanizing agent, polyamine compound, a polyol compound, a polycarboxylic acid compound, each of a polyfunctional epoxy compound, dibasic acid anhydride or the 2 hydrochloric-acid anhydride compound of many organic functions, a metal oxide, benzoic acid, a cumic acid, and a higher fatty acid -- according to the functional group in fluorine-containing elastomer, the selection use of ammonium salt, the hydrochloride of amine, etc. can be carried out suitably.

ii) by using fluorine-containing elastomer of this invention which introduced the functional group into fluorine-containing elastomer on the occasion of the blend with fluorine-containing elastomer and the other non-fluorine elastomer Furthermore, it can deal in the physical characteristic, the chemical resistance, the outstanding plasticity, and outstanding low temperature nature which were not looked at by the conventional fluorine elastomer by performing the same vulcanization operation as the above. As said non-fluorine elastomer, each elastomer of acrylic, a silicone system, an epichlorohydrin system, a NBR system, and a urethane system is raised preferably. Moreover, by choosing the kind and vulcanizing agent of the functional group of fluorine-containing elastomer, and a non-fluorine elastomer, and the vulcanization method, and controlling mutual vulcanization velocity and crosslinking density ***** of functional group content fluorine-containing elastomer / a non-fluorine elastomer system can be performed, and the blend which was [compression set / mechanical hardness,] excellent can deal in a bridge formation thing, the quantity of the functional group at the time of bridge formation or the blend with other non-fluorine elastomers, and a blend constructing a bridge using the functional group of the above functional group content fluorine-containing elastomer -- 0.01-10mol % -- it is 0.1-5mol % preferably. The 3rd of this invention is related with the thermoplastics constituent which consists of said functional group content fluorine polymer and heat-resistant thermoplastics, that is, the thermoplastics constituent of this invention -- 0.1 to 99% (weight % --) of (D) functional group content fluorine-containing polymer They are that it is the same as that of the following, and the thing which consists of a blend thing obtained by mixing 1 to 99.9% of the heat-resistant thermoplastics which has the crystalline melting point or glass

transition point beyond (E)150 degree C. One or more sorts of things chosen from the fluorine polymer which exists and is shown in Claim 1 of this invention as this functional group content fluorine-containing polymer (D) are used.

When performing the blend of heat-resistant thermoplastics and fluorine-containing polymer, by the conventional method, the constituent which was not obtained and which can give homogeneous mold goods easily can be offered by using the functional group content fluorine polymer of this invention for fluorine-containing polymer.

Functional group content fluorine-containing polymer (D) is a fluorine polymer expressed with Claim 1 of this invention. Although the functional group in functional group content fluorine-containing polymer is mainly chosen by the kind of heat-resistant thermoplastics (E) to blend, a hydroxy group especially with high reactivity with thermoplastics (E) (polymer of Claim 4), What has a carboxy group (polymer of Claim 5), a carboxy ester group (polymer of Claim 6), and a glycidyl group (polymer of Claim 7) is used preferably.

Although the functional group concentration in functional group content fluorine-containing polymer (D) can be freely chosen by the kind of thermoplastics (E), the presentation rate of (D) and (E) and the purpose, and a use when blending superfluous functional group concentration with thermoplastics desirably, in order to improve a distributed state for Reasons of characteristics, such as the heat-resisting property of a constituent, chemical resistance, and mechanical physical properties, -- the minimum -- a required quantity is included -- ****ing -- functional group content fluorine-containing polymer (D)

They are 0.05 - 15mol % to 0.01 - 30mol % and profit preferably [the content of a functional group content fluorine-containing monomer (A) is desirable to all the inner use monomers, and].

Although functional group content fluorine-containing polymer (D) can be suitably chosen by the purpose of using the kind of heat-resistant thermoplastics (E) to blend, a constituent, and a Plastic solid, and a use, a desirable thing fulfills the following conditions.

1) In order for the melting kneading temperature of heat-resistant thermoplastics (E) to have many things of the range of 200-380 degrees C and to deal in a good distributed state generally, as for fluorine-containing polymer (E), what is fused below 380 degrees C is desirable, and what is fused below especially 350 degrees C is desirable. Thereby, thermoplastics and the kneading temperature at the time of a blend can be chosen broadly.

2) Fluorine-containing polymer (D) itself needs to have the thermal stability (heat-resisting property) which can be equal to kneading and shaping in high temperature. Even if it decomposes slightly at the time of kneading, as long as an effect is accepted, it is unavoidable, but you should have 200 degrees C of heat-resisting properties of 250 degrees C or more preferably as it is low. It depends for a heat-resisting property on the kind and composition ratio of the mainly used monomer. high draw carbon system monomers other than ethylene, propylene, and isobutylene -- for example, When using alkyl vinyl ether, alkyl vinyl ester, and an aryl compound, it is desirable to limit the rate in these polymer to less than 20 mol %, and carrying out to less than 10 mol % especially is recommended.

The heat-resisting property in this invention means the temperature of the decrease of

weight 1% by measurement (10-degree-C **** [A part for /]) of the thermobalance in the air.

3) the capability that the chemical resistance and the oil resistance of fluorine-containing polymer itself, and solvent resistance are high, and those features can be given to a blend constituent with thermoplastics (E) -- **** -- it is required to be.

As desirable fluorine-containing polymer (D) for fulfilling these conditions One is a functional group content fluorine-containing copolymer which makes a principal component tetrafluoroethylene (or chlorotrifluoroethylene) shown by Claim 13 of this invention first, [what introduced the functional group content monomer into what is called FEP and PFA, and E(C) TFE / desirable especially] also in it preferably They are PFA, an E(C) TFE type functional group content fluorine-containing copolymer, and the ethylene tetrafluoroethylene (or chlorotrifluoroethylene) system copolymer of a presentation as most preferably shown in Claim 16.

[the 2nd desirable thing which fluorine-containing polymer (D) has] Are the functional group content fluorine polymer of a vinylidene fluoride system as shown in Claim 11, and in detail [what introduced the functional group into PVdF like Claim 14, and the thing which introduced the functional group into the copolymer which made the principal component vinylidene fluoride as shown in Claim 15 / desirable especially] preferably A presentation as shown in PVdF type the fluorine polymer and Claim 18 of Claim 14 That is, fluorination vinylidene tetrafluoroethylene, Fluorination vinylidene tetrafluoroethylene chlorotrifluoroethylene, They are functional group content fluorine-containing copolymers, such as fluorination vinylidene tetrafluoroethylene hexafluoropropylene, fluorination vinylidene chlorotrifluoroethylene, and fluorination vinylidene hexafluoropropylene.

Moreover, the functional group content fluorine-containing polymer in this invention may also be which description of resin and an elastomer by the kind and composition ratio of the monomer to be used. The latter is the meaning of a grade which has a glass transition temperature lower than a room temperature, and the distinction of resin and an elastomer can choose either for the purpose of a blend. A case to deal in a shock-proof improvement of thermoplastics or an elastomeric blend thing uses elastomeric functional group content fluorine-containing polymer.

[the reasonable desirable functional group content fluorine-containing elastomer which can attain said purpose in the fluorine-containing polymer (D) of this invention] They are the fluorine-containing copolymer which makes a principal component tetrafluoroethylene of the presentation shown by Claim 17, and the fluorine-containing copolymer which makes a principal component vinylidene fluoride of the presentation shown by Claim 19.

The molecular weight of the functional group content fluorine-containing polymer in this invention is comparable as general fluorine-containing resin and fluorine-containing elastomer except PTFE it is usually said that are the millions or more amounts of polymers, and is 2,000-1,000,000 in a number average molecular weight. Too low molecular weight spoils the heat-resisting property of a constituent, or reduces mechanical physical properties depending on composition ratio. On the other hand, since moldability falls, too high molecular weight is not desirable. Desirable molecular weight is about 5000 to 750000 number average molecular weight, and is 10000 to about 500000 especially preferably.

As for functional group content fluorine-containing polymer (D), in this invention, a crystalline melting point or glass transition temperature is blended with thermoplastics (E) of 150 degrees C or more. As thermoplastics, for example Polyacetal, polyamide, polycarbonate, Polyphenylene ether, aromatic polyester, aromatic series polyester amide, They are aromatic series azomethine, poly arylene sulfide, poly SARUHON and polyether sulphone, poly ketone and polyether ketone, polyether imide, polyamidoimide, poly methyl pentene, polyether nitrile, etc.

A thing desirable also in it has the high heat-resisting property of a 1 thermoplastics (E) simple substance.

That is, it is required not to reduce the thermal stability of a constituent in the case of fluorine-containing polymer and a blend, again since thermoplastics's (E) own heat-resisting property is high If a general modifier and an additive are used in order to improve the shock resistance and chemical resistance of (E) It is a thing excellent in the resin that the heat-resisting property of a constituent falls and addition of heat-resistant high fluorine-containing polymer is desired, 2 mechanical hardness, and dimensional stability. What can reform them of a fluororesin, the thing which can give the workability which is the thing excellent in 3 moldability and was excellent in the constituent with fluorine-containing polymer, It comes out, and it is, for example, aromatic polyester, polyamide, polyamidoimide, poly arylene sulfide, poly ketone, polyether nitrile, polycarbonate, polyphenylene ether, poly SARUHON, polyether imide, polyimide, etc. are the desirable objects of this invention.

The poly arylene sulfide expected a shock-proof improvement strongly without generally still more specifically spoiling a heat-resisting property and chemical resistance, The polyamide expected improvement of solvent resistance, especially gasohol-proof nature, etc. when used as a charge of autoparts material, Since it excels in shaping workability or dimensional stability at the rate of high elasticity also especially the aromatic polyester which improvement in the moldability of fluorine polymer and mechanical physical properties can expect by addition, and in it, By raising compatibility with fluorine polymer, the liquid crystal polyester which forms the anisotropic melt phase which can expect improvement with large mechanical physical properties of fluorine polymer, moldability, dimensional stability, and load deflection temperature can raise as a desirable object especially.

When the reactivity of the functional group content fluorine-containing polymer (D) of this invention and thermoplastics (E) is taken into consideration, on the other hand, [polyphenylene SAIFAIDO] Polyamide contains a thio rate machine (or thiol group), an amino group, a carboxy group, amide binding, and aromatic polyester include a hydroxy group, a carboxyl group, and an ester bond, and the possibility of a reaction with the functional group in the fluorine-containing polymer (D) of this invention is the object in which it is high and the meaning is also desirable.

The functional groups in the functional group content fluorine-containing polymer (D) in this invention are a hydroxy group, a carboxy group, a carboxy ester group, and a glycidyl group. When heat-resistant thermoplastics (E) is aromatic polyester, generally these functional groups The ester bond of a principal chain, and the hydroxy group of an end, In the case of a carboxyl group and polyamide (PA), in the case of the amino group of amide binding of a principal chain, or an end, a carboxyl group, and poly arylene sulfide, reactivity with the thio rate machine (or thiol group) of an end is high. That is, by

carrying out melting kneading of functional group content fluorine-containing polymer (D) and the thermoplastics (E) The principal chain of thermoplastics (E), a part of end, a part of resultant (2) fluorine-containing polymer (D) that reacted, and some thermoplastics (E) (1) the obtained constituent [the functional group of (1) functional-group content fluorine-containing polymer (D)] the constituent (3) which the same chemical reaction was caused, and the resultant acted as a compatibility modifier of the constituent containing an unreacted thing, and was made -- especially When a chemical reaction is not caused but ** also introduces a functional group to fluorine-containing polymer, it is presumed that interface compatibility with thermoplastics (E) and an interface adhesive property may be existed in one form of the constituents by which property modification was carried out. This invention is not limited by this although the mechanism from which good dispersibility is mutually acquired as mentioned above with the blend with functional group content fluorine-containing polymer (D) and thermoplastics (E) is not clear. In order to raise compatibility with the functional group content fluorine-containing polymer of this invention, or reactivity, denaturalizing thermoplastics (E) according to a conventional method is not eliminated from this invention, either. Moreover, polymer components (F) other than thermoplastics (E) and functional group content fluorine-containing polymer (D) can be included in the resin composition thing of this invention.

The functional group content fluorine-containing monomer of a fluorine polymer as shows Claim 1 of this invention the desirable component of (F) to (A), In addition, are the functional group except a functional group content monomer the fluorine-containing polymer which it does not have, and as an especially desirable thing of (F) (1) PTFE (a **** copolymer is included for TFE and copolymerizable fluorine-containing olefin less than 1weight %), TFE / perfluoro (alkyl vinyl ether) copolymer (PFA), The perfluoro system fluororesin or elastomer like a TFE/HFP copolymer (FEP), and TFE / perfluoro (alkyl vinyl ether) / HFP ternary polymerization object, (2) The mole composition ratio of the ethylene pairs TFE and CTFE known in the name of common names ETFE and ECTFE is 2 to 3-3 pairs two, and -- the 3rd fluorine-containing monomer which can carry out copolymerization to them receives ethylene, TFE, and/or the CTFE monomer whole quantity -- 0-15mol % -- the resin-like copolymer contained -- Or in about 40-90mol % and TFE, and/or CTFE, the about 0.1-20mol 3rd fluorine-containing monomer% as the elastomer-like copolymer of about 10-60mol% of presentation, and the 3rd fluorine-containing monomer [ethylene] $\text{CH}_2=\text{CZ}_7(\text{CF}_2)$ k"Z8 (Z7 -- H or F, and Z8 -- H or F --) k "integer [of 1-10] and $\text{CF}_2=\text{CF}(\text{CF}_2)$ 1" Y4 (Y4 -- H --) F and 1" -- the integer of 1-10, and $\text{CF}_2=\text{CFO}(\text{CF}_2)$ m"Y5 (Y5 -- H --) At least one sort (F and m") shown by the integer of 1-6 and $\text{CH}_2=\text{C}(\text{CF}_3)_2$ is used. And tetrafluoroethylene / 40-70mol of propylene copolymer, for example, tetrafluoroethylene, %, The copolymer, (3) PVDF, and the VDF system copolymer ([VDF / TFE and]) of the shape of an elastomer which consists of 30-60mol of propylene % It is the shape of resin or an elastomer-like copolymer with at least one sort of fluorine-containing olefin chosen from fluorine-containing olefin, such as CTFE, HFP, $\text{CH}_2=\text{C}(\text{CF}_3)_2$, or $(\text{CF}_3)_2\text{C}=\text{O}$. [the ternary polymerization object of a VDF/HFP copolymer, a VDF/CTFE copolymer, VDF/TFE/HFP, or CTFE] Usually, in VDF, about 20-80mol % and TFE become less than [abbreviation 40 mol %], HFP becomes about 10-60mol %, and CTFE serves as an

elastomer in the about 15-40mol% of range.

(4) As others, fluorine-containing resin or elastomers, such as polychlorotrifluoroethylene resin (PCTFE) and Pori (fluoro alkyl alpha-displacement acrylate) (substituents are a hydrogen atom or a methyl group, a fluorine atom, and a chlorine atom), are raised.

Namely, it sets to the constituent of three components of the fluorine-containing polymer (F) which does not contain functional group content fluorine-containing polymer (D), thermoplastics (E), and said functional group. The functional group content fluorine-containing polymer in the constituent (D) and some resultants of the thermoplastics (E) can act as a compatibility modifier to the portion of the fluorine-containing polymer (F) and thermoplastics (E) which do not contain other functional groups. [in in other words blending fluorine-containing polymer (F) and thermoplastics (E) / add functional group content fluorine-containing polymer (D), and] by carrying out a melting blend the dispersibility which a compatibilizer is formed into a constituent and acquired by the blend thing of mere fluorine-containing polymer (F) and thermoplastics (E) -- further -- mechanical physical properties, chemical resistance, etc. -- a constituent -- ***** -- things are made.

Therefore, as for the functional group content fluorine-containing polymer (D) added in these constituents for dispersibility improvement, what has the high fluorine-containing polymer (F) which does not contain a functional group and compatibility is desirable. For example As fluorine-containing polymer (F) To the presentation chosen from a perfluoro system fluororesin or an elastomer as shown above (1) the same when blending with the fluorine-containing polymer and thermoplastics (E) which are chosen from the perfluoro system fluororesin or elastomer of the above (1), [a functional group] Fluorine-containing polymer (F) is chosen for the introduced functional group content fluorine-containing polymer again from the groups of the ethylene / tetrafluoroethylene (or chlorotrifluoroethylene) system polymer of the above (2), and a propylene / tetrafluoroethylene copolymer, and it is thermoplastics (E).

[what introduced the functional group into the presentation similarly chosen from the groups of (2) when blending] When [moreover,] choosing fluorine-containing polymer (F) from the group of the vinylidene fluoride system polymer of the above (3) and blending with (E) It is most desirable to add, respectively what is chosen from the functional group content fluorine polymer which makes a principal component vinylidene fluoride as shown in Claim 11 on the effect of the improvement in dispersibility. Although the amount of addition of functional group content fluorine-containing polymer (D) effective for the improvement in dispersibility changes on the occasion of the blend with fluorine-containing polymer (F) and thermoplastics (E) with each kind of fluorine-containing polymer (F) and thermoplastics (E), the mixing ratio, the purposes, etc. Generally, it is 0.5 to 50 weight % to the whole constituent, and it is 0.5 to 30 weight % preferably, and is especially effective enough at 1 to 20 weight %.

It is required to perform at least a blend of three components which added the fluorine-containing polymer (F) which does not contain a functional group in functional group content fluorine-containing polymer (D), thermoplastics (E), or said presentation further in the state of melting and a flow more than the crystalline melting point of thermoplastics or glass transition temperature. During a blend, although it is desirable for functional group content fluorine-containing polymer to be also a molten state, melt viscosity is high or may hold unmelting nature for the Reason which is bridge formation

nature.

The thermoplastics constituent of this invention comes to mix with functional group content fluorine-containing polymer (D) as shown by Claim 1 the thermoplastics (E) which has the crystalline melting point or glass transition temperature of 150 degrees C or more, and the presentation is (D)0.1-99% and (E)1-99%.

Among these, when considering it as (D)0.1-40% and (E)60-99.9%, character which is the faults of much thermoplastics, such as shock resistance, sliding nature, chemical resistance, and moldability, can reform by fluorine polymer. Moreover, when considering it as (D)40-99% and (E)1-60%, the hardness of fluorine polymer, load deflection temperature, moldability, and dimensional stability can reform with thermoplastics. When (D) is less than 0.1% in the bulk density of a resin composition thing, and when (E) is less than 1%, said property modification effect will become dissatisfied.

Since the content and its kind in inside of the constituent of functional group content fluorine-containing polymer differ from each other with the kind of functional group, concentration, a basic component, molecular weight, etc., it cannot determine uniformly and chooses according to the kind of thermoplastics and the purpose of a blend which are blended within the limits of the above.

The desirable resin composition thing of this invention is a constituent which consists of the fluorine-containing polymer, the Pori arylene sulfide, polyamide, aromatic polyester, or polycarbonate containing hydroxyl, a carboxyl group, and a glycidyl group.

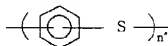
Especially although Pori arylene sulfide is excellent in the heat-resisting property and the mechanical property, it has the character in which shock resistance is inferior. What contains reactant high hydroxyl with the thio rate machine (or thiol group) of the end of a polyphenylene sulfide as fluorine-containing polymer (D) in the blend with Pori arylene sulfide and functional group content fluorine-containing polymer (D) (polymer of Claim 4), When fluorine-containing polymer with a glycidyl group (polymer of Claim 7) raises dispersibility, it is desirable and fluorine-containing elastomer-like polymer is desirable especially in respect of shock-proof improvement also in it.

[the amount] although the amount of functional groups in fluorine-containing elastomer changes with fluorine-containing elastomer, kinds, the mixing ratio of Pori arylene sulfide, etc. the mol of the use monomer of fluorine-containing elastomer -- as opposed to a number -- 0.01-30mol % -- desirable -- 0.01-20mol % -- it is about 0.05-10 mol % especially preferably.

The inside of the fluorine polymer of a vinylidene fluoride system of a presentation as shown by Claim 19 as an example of a functional group content elastomer, The thing of hydroxyl or a glycidyl group is preferably raised for a functional group among the fluorine polymers to which the functional group made the principal component the thing of hydroxyl or a glycidyl group, or tetrafluoroethylene of the presentation as shown by Claim 17. Especially A fluoridation vinylidene hexafluoropropylene copolymer, a fluoridation vinylidene tetrafluoroethylene hexafluoropropylene copolymer, What introduced tetrafluoro ethylene propylene rubber hydroxyl or a glycidyl group is raised especially preferably.

As PPS used by this invention, it was obtained by a well-known method which is indicated to JP,S45-3368,B.

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the repetition unit come out of and shown -- more than 70 mol % -- what is included is desirable. furthermore -- as a repetition unit -- p-phenylene sulfide unit -- more than 70 mol % -- PPS to contain is used especially suitably. Under the present circumstances, if it is an unit copolymerizable as remaining repetition units, there will be no restriction. For example, o-phenylene sulfide unit, m-phenylene sulfide unit, A diphenyl sulfide ether unit, a diphenyl sulfide sulfone unit, a diphenyl sulfide ketone unit, a biphenyl sulfide unit, a naphthalene sulfide unit, 3 organic-functions phenylene sulfide unit, etc. are raised. Even if block copolymerization is carried out, random copolymerization of these copolymers may be carried out.

As a desirable example of PPS, Pori (p-phenylene sulfide), The Pori (p-phenylene sulfide)-Pori (m-phenylene sulfide) block copolymer, the Pori (p-phenylene sulfide)-polysulfone block copolymer, and the Pori (p-phenylene sulfide)-polyphenylene sulfide sulfone copolymer are raised.

Moreover, whether it carries out bottom oxygen bridge formation of oxygen coexistence even if it is a normal chain-like thing, or it gives heat-treatment under inert gas atmosphere, you may be the mixture of such structures further regardlessly.

Moreover, in order to raise further compatibility with the functional group content fluorine-containing polymer used by this invention, you may introduce a reactant high functional group into PPS. As a functional group introduced, an amino group, a carboxylic acid group, a hydroxyl group, etc. are suitable, and the method of introducing by the polymer reaction of the method and PPS which carry out copolymerization of the halogenated-aromatics compound which contains these functional groups as the introductory method, and the low molecular weight compound containing a functional group etc. is raised.

Moreover, said PPS may reduce sodium ion by performing deionization treatment (acid cleaning, hot water cleaning, etc.).

Although the presentation of functional group content fluorine-containing elastomer and Pori arylene sulfide can be used in the range of 0.1 to 40% of functional group content fluorine-containing elastomer, and 60 to 99.9% of Pori arylene sulfide They are 5 to 30% of functional group content fluorine-containing elastomer, and 70 to 95% of Pori arylene sulfide especially preferably. Shock-proof improvement sufficient in the case where functional group content fluorine-containing elastomer is less than 5% cannot be performed, but if it exceeds 30% conversely, the fall of mechanical hardness will become remarkable.

The constituent which consists of the polyphenylene sulfide and the functional group content fluorine-containing polymer which were obtained as mentioned above can give an outstanding mechanical property which is not acquired only by blending the fluorine-containing polymer which does not only contain a functional group, especially shock resistance to mold goods.

Moreover, since the heat-resisting property which fluorine-containing polymer originally has, chemical resistance, sliding nature, the heat-resisting property that a polyphenylene sulfide originally has, and machine characteristics can be served both as and offered. It is useful especially as molding materials, such as electricity and electronic parts using a heat-resisting property and an electrical property, parts for cars using sliding nature, a pipe for chemical plants using chemical resistance, and gear parts for valve pumps.

Polyamide resin is excellent in high intensity, high toughness, and workability, and is widely used for the hose, the inner tube, the pipe, etc. On the other hand, although generally excelled also in oil resistance, the oil resistance (gasohol-proof nature) at the time of using the gasoline which contains lower alcohol especially weakly to the solvent of an alcoholic system worsens, and volume swelling and a fuel penetration become large and cause material degradation, such as strength reduction.

By blending the functional group fluorine-containing polymer (D) of this invention with polyamide resin Moreover, by adding functional group content fluorine-containing polymer (D) in the blend thing of fluorine-containing polymer (F) and polyamide resin, it can deal in the constituent which improved the solvent resistance of said polyamide resin, and gasohol-proof nature.

In the constituent of functional group content fluorine-containing polymer (D) and polyamide, as fluorine-containing polymer (D) Fluorine-containing polymer with a thing (polymer of Claim 5) or a glycidyl group with the carboxyl group considered that reactivity is high by amide binding of the principal chain of polyamide, the amino group of an end, or the carboxyl group (polymer of Claim 7) is desirable. although the amount of functional groups changes with the kind of fluorine-containing polymer and each polyamide resin, mixed rates, the purposes, etc. -- the use mol of fluorine-containing polymer -- as opposed to a number -- 0.01-30mol % -- desirable -- 0.01-20mol % -- it is about 0.05-10 mol % especially preferably.

As functional group content fluorine-containing polymer (D), either of the polymer of the shape of resin or the shape of an elastomer can be chosen by the purpose of use and a use. [if thermofusion is possible for the case of fluorine-containing resin-like polymer, will not be limited, but] Especially a fluorine polymer of 280 degrees C or less has a fusing point comparatively low in it, in order to prevent the heat deterioration of polyamide in the constituent at the time of carrying out melting kneading with polyamide and manufacturing a constituent, namely, desirable also in 300 degrees C or less. A functional group specifically among the ethylene tetrafluoroethylene (or chlorotrifluoroethylene) copolymers of the presentation shown by Claim 16 The thing of a carboxyl group or a glycidyl group. The thing of a carboxyl group or a glycidyl group has a desirable functional group among the vinylidene fluoride system polymers of Claim 11. A vinylidene fluoride system polymer in more detail PVdF of Claim 14, The fluoridation vinylidene tetrafluoroethylene copolymer of the presentation shown by Claim 18, A fluoridation vinylidene hexafluoropropylene copolymer, a fluoridation vinylidene chlorotrifluoroethylene copolymer, What introduced the carboxyl group or the glycidyl group into each of the fluoridation vinylidene tetrafluoroethylene hexafluoro ethylene copolymer and the fluoridation vinylidene tetrafluoroethylene chlorotrifluoroethylene copolymer is raised preferably.

Moreover, the copolymer which makes a principal component tetrafluoroethylene as shown by Claim 17 which contained the carboxyl group and the glycidyl group as fluorine-containing elastomer-like polymer, and a vinylidene fluoride copolymer as shown by Claim 19 are raised preferably, respectively.

Moreover, it can deal in the constituent which improved dispersibility and chemical resistance also by adding functional group content fluorine-containing polymer (D) in the case of the blend with the fluorine-containing polymer (F) and polyamide resin which do not contain a functional group. The constituent which added the polymer of Claim 16 of

carboxyl or glycidyl group content in the blend thing of ETFE (or ECTFE) and polyamide as an example of the combination of a constituent. Are chosen from the vinylidene fluoride system polymers shown in the blend thing of PVdF and polyamide resin by Claim 11. The constituent and vinylidene fluoride which added the polymer with carboxyl or a glycidyl group are made indispensable. Tetrafluoroethylene, hexafluoropropylene, [the carboxyl group or glycidyl group chosen from the vinylidene fluoride system polymers shown in the blend thing of the vinylidene fluoride system polymer and polyamide of the shape of resin, or the shape of an elastomer which consists of at least one sort chosen from chlorotrifluoroethylene by Claim 11] The constituent which added the polymer which it has is hung up preferably.

In the added constituent, functional group content fluorine-containing polymer (D) in the blend thing of the fluorine-containing polymer (F) and polyamide which do not contain a functional group Dispersibility, Although the content of (D) effective for improvement in compatibility changes with kinds, mixed rates, etc. of fluorine-containing polymer (F) and polyamide, generally it is 1 to 20% preferably [it is desirable and] to 0.5-30, and profit 0.5 to 50% to the whole constituent.

Polyamide resin usually The following type The line diamine and the following type which are shown by $\text{H}_2\text{N}-(\text{CH}_2)_p-\text{NH}_2$ (the inside of a formula and p " are the integers of 3-12) What was manufactured by condensation with the line carboxylic acid shown by $\text{HO}_2\text{C}-(\text{CH}_2)_q-\text{CO}_2\text{H}$ (the inside of a formula and q " are the integers of 2-12), and the thing manufactured by the ring opening polymerization of lactam can be used. As a desirable example of these polyamide, there are nylon 6 and 6, nylon 6 and 10, nylon 6 and 12, nylon 4 and 6, nylon 3 and 4, nylon 6 and 9, nylon 6, Nylon 12, Nylon 11, nylon 4, etc. Moreover, nylon 6/6, 10, nylon 6/6, 12, nylon 6/4, 6, nylon 6/12, nylon 6/6, 6, nylon 6/6, 6/6, 10, nylon 6/4, 6/6, 6, nylon 6/6, 6/6, 12, nylon 6/4, 6/6, 10, nylon 6/4, Copolymerization polyamide, such as 6/12, is used.

Furthermore, Nylon 6/6T (T is a terephthalic acid component), terephthalic acid, The half-aromatic polyamide obtained from aromatic dicarboxylic acid like isophthalic acid, meta-xylene diamine, or alicycle group diamine and the polyamide which are obtained from meta-xylene diamine and said line carboxylic acid can be raised.

[the constituent which added functional group content fluorine-containing polymer (D) in the blend thing of the fluorine-containing polymer (F) and polyamide which do not contain the constituent or functional group which consists of above functional group content fluorine-containing polymers (D) and polyamide] As [obtain / only by blending the fluorine-containing polymer which does not only contain a functional group]

Chemical resistance, low-temperature impact resistance, and a mechanical property can be given to mold goods. The reformed gasoline which contains alcoholic (for example, methanol, ethanol, etc.) methyl t-butyl ether etc. especially, It is useful as a material which has the outstanding chemical resistance to an acid etc., and impermeability, and useful on a Plastic solid, for example, a hose, an inner tube, a pipe, a seal, a gasket, packing, a sheet, a film, etc. Moreover, it can become the autparts of which the chemical resistance especially to gasoline and methanol mixed gasoline and impermeability are required, for example, a fuel piping hose, an inner tube, a gasket, etc. with a useful material.

Perfluoro system fluororesins, such as PTFE, FEP, and PFA, and ETFE, [fluororesins, such as ECTFE, PVdF, and vinylidene fluoride system copolymers (for example,

fluoridation vinylidene tetrafluoroethylene copolymer etc.),] Although generally excelled in a heat-resisting property, chemical resistance, weatherability, an electrical property, etc., compared with crystalline heat-resistant thermoplastics, it is inferior to a mechanical property, the physical heat-resisting property shown with load deflection temperature, dimensional stability, etc. in many cases.

By changing to fluorine-containing resin of these former, and blending aromatic polyester or polycarbonate also especially heat-resistant thermoplastics (E) and in it using functional group content fluorine-containing resin (D) of this invention Moreover, when blending fluorine-containing resin (F), conventional aromatic polyester, or conventional polycarbonate, it can deal in the constituent which improved the mechanical property, load deflection temperature, and dimensional stability which a fluoro-resin simple substance has by adding functional group content fluorine-containing polymer (D).

In the constituent of aromatic polyester or polycarbonate, and functional group content fluorine-containing polymer (D), as fluorine-containing polymer (D) A thing with a hydroxy group or a carboxyl ester group, and a glycidyl group preferably also in it Especially the fluorine-containing polymer with a hydroxy group (polymer of Claim 4) carboxyl ester group (fluorine polymer of Claim 6) considered that the ester group of the principal chain of aromatic polyester or the carbonate machine of the principal chain of polycarbonate, and an ester exchange reaction occur easily is desirable. [content] although the content of a hydroxy group, a carboxyl ester group, or a glycidyl group changes with the kind of aromatic polyester and polycarbonate, the kind of fluorine-containing polymer, composition ratios, etc. as opposed to the amount of all [used] in functional group content fluorine-containing polymer -- 0.01-30mol % -- desirable -- 0.01-20mol % -- it is about 0.05-10 mol % especially preferably.

[in the case of the constituent of two components of functional group content fluorine-containing polymer, aromatic polyester, or polycarbonate, as functional group content fluorine-containing polymer, can choose many things by the purpose or a use, but] PTFE, FEP, PFA, ETFE, ECTFE, PVdF, vinylidene fluoride system copolymer (VdF-TEFE copolymer etc.) resin, What introduced the hydroxy group or the carboxyl ester group into each of polymers, such as PCTFE, is desirable. [what introduced hydroxyl or a carboxyl ester group into each of PFA, ETFE, ECTFE, PVdF, and PCTFE also in it] Especially, it is desirable and the mechanical property, the load deflection temperature, dimensional stability, and moldability which the fluoro-resin simple substance which carries out considerable, respectively has can be improved more effectively.

In functional group content fluorine-containing polymer (D), aromatic polyester, or the constituent by two components with polycarbonate a presentation effective for improvement of the mechanical property of fluorine-containing polymer, load deflection temperature, dimensional stability, and moldability -- functional group content fluorine-containing (polymer D) 50-99%, aromatic polyester, or (Polycarbonate E) 1- they are (D)60-97% and (E)3-40% preferably 50%.

In the case of the constituent of three products which add the functional group content fluorine-containing polymer (D) of this invention in the case of the blend of the above conventional fluorine-containing resin (F), aromatic polyester, or polycarbonate The functional group content polymer (D) to add is preferably chosen by what has high fluorine-containing resin (F) without the functional group in a constituent and compatibility, and as a combination of a concrete constituent a perfluoro system

fluororesin (for example, PTFE and FEP --) The constituent which added the fluorine-containing polymer which introduced hydroxyl or a carboxyl ester group into the polymer chosen as PFA, etc. aromatic polyester, or a blend thing with polycarbonate from a perfluoro system fluororesin, [ETFE (or ECTFE), aromatic polyester, or a blend thing with polycarbonate] The hydroxy group of a presentation as shown by Claim 16, or the constituent which added carboxyl ester group content ethylene / tetrafluoroethylene (or chlorotrifluoroethylene) copolymer, As [showed / in PVdF or vinylidene fluoride system copolymer resin, aromatic polyester, or a blend thing with polycarbonate / Claim 14 and 15] The constituent which added the hydroxyl chosen from the polymer which makes vinylidene fluoride a principal component, or the vinylidene fluoride system polymer (in this case, you may be whichever of the shape of resin or the shape of an elastomer) of carboxyl ester group content is raised especially preferably.

In the added constituent, functional group content fluorine-containing polymer (D) in conventional fluorine-containing resin, aromatic polyester, or the blend thing of polycarbonate Dispersibility, Although the content of ** (D) effective for improvement in compatibility changes with the kinds and the mixed rates of fluorine-containing resin, aromatic polyester, and polycarbonate, generally it is 1 to 20% especially preferably 0.5 to 30% preferably 0.5 to 50% to the whole constituent.

In the constituent by three components which added functional group content fluorine-containing polymer (D) in fluorine-containing resin (F), aromatic polyester, or the blend thing of polycarbonate (E) [a presentation effective for improvement of the mechanical property of fluorine-containing polymer, load deflection temperature, dimensional stability, and moldability] Functional group content fluorine-containing polymer (D) 0.5 to 50%, aromatic polyester, or (Polycarbonate E) 1-50%, the remainder -- fluorine-containing resin (F) (however, the total quantity of (D) and (F) -- 50 to 99%) -- desirable -- (D)1-30%, (E)3-40%, and the remainder -- (F (however, (D) (F)))

The total quantity is 60 to 97%.

By carrying out the dissolution blend of elastomer-like a fluorine polymer and thermoplastics (E) in the functional group content polymer (D) of this invention, a chemical reaction arises partially and it can deal in a thermoplastic elastomer composition in the specific composition ratio range with (D) and (E). Specifically [hydroxyl content or carboxyl ester group content fluorine-containing elastomer] by carrying out a melting blend in aromatic polyester or polycarbonate, and a certain specific composition ratio range especially as functional group content fluorine-containing polymer of this invention A chemical reaction can be partially carried out by an ester exchange reaction, and it can deal in the thermoplastic elastomer composition which it had in accordance with high temperature flowability and the rubber elasticity as an elastomer as thermoplasticity. In this thermoplastic elastomer composition, [hydronalium KISHIRU or a carboxyl ester group content elastomer] The polymer which made the principal component tetrafluoroethylene of the presentation indicated to Claim 17, Especially, the vinylidene fluoride of the presentation indicated to Claim 19 is preferably used by the polymer made into the principal component, and it [the content of a hydroxy group or a carboxyl ester group] as opposed to all the use monomers of fluorine-containing elastomer -- 0.01-30mol % -- desirable -- 0.01-20mol % -- it is 0.05-10mol % especially preferably.

Hydroxy **** which can double and have the high temperature flowability as a thermoplastic elastomer and rubber elasticity [the mixed rate with carboxyl ester group

content fluorine-containing elastomer, aromatic polyester, or polycarbonate] Hydronalium KISHIRU or 50 to 99.9% of carboxyl ester group content fluorine-containing elastomer, They are hydronalium KISHIRU or 70 to 98% of carboxyl ester group content fluorine-containing elastomer, aromatic polyester, or 2 to 30% of polycarbonate preferably to aromatic polyester or the constituent of 0.1 to 50% of polycarbonate, and profit. Moreover, in this composition ratio range, it can deal in the thermoplastic elastomer of various hardness by choosing the mutual mixing ratio. Polycarbonate has chemical resistance and a fault inferior to especially alkali resistance and solvent resistance, although use has spread in the car or the construction field for the features, such as the mechanical hardness, shock resistance, and weatherability. It can deal in the constituent which improved chemical resistance more effectively without reducing mechanical physical properties remarkably by blending the fluorine-containing polymer which has a hydroxy group among the functional group content fluorine-containing polymer of this invention in polycarbonate by the same method as a chemical-resistant improvement of polyamide.

As aromatic polyester used in the constituent of this invention For example, adipic acid, terephthalic acid, 2, 6-naphthalene dicarboxylic acid, A dibasic acid and ethyne glycols, such as 4 and 4'-biphenyl dicarboxylic acid, Trimethylene glycol, tetramethylene glycol, pentamethylene glycol, Hexamethylene glycol, 1, 4-cyclohexane dimethanol, a condensate (for example, polyethylene terephthalate --) with dihydric alcohol, such as bisphenol A The aromatic polyester (liquid crystal copoly ester) which forms anisotropic melt phases, such as polybutylene terephthalate, Pori 1, 4-cyclohexane-dimethylene-terephthalate, Pori [2, and 2-propane bis(4-phenyl call / isophthalate)], is raised. Moreover, the polycarbonate used in the constituent of this invention is obtained by a reaction with a bisphenol compound, carbonyl chloride, or carbonic acid diester. Although 2 and 2-bis(4-hydroxyphenyl) propane (it abbreviates to bisphenol A hereafter) is desirable especially as a bisphenol compound, other bisphenol compounds may replace some or all of bisphenol A. As bisphenol compounds other than bisphenol A For example, hydroquinone, resorcinol, 4, and 4'-dihydroxydiphenyl, Bis(4-hydroxyphenyl) alkane, bis(4-hydroxyphenyl) cycloalkane, Bis(4-hydroxyphenyl) sulfide, bis(4-hydroxyphenyl) ether, Bis(4-hydroxyphenyl) ketone, bis(4-hydroxyphenyl) sulfone, bis(4-hydroxyphenyl) sulfoxides or these alkylation objects, an aryl substitution product, a halogenation object, etc. are raised.

Also in them, liquid crystal polyester has the performance which was most excellent in thermal properties, such as mechanical properties, such as hardness and an elastic modulus, and load deflection temperature, dimensional stability, etc. in itself with the orientation, and shows high flowability at the time of melting. An orientation is carried out in a constituent by furthermore carrying out a melting blend with other polymer. The same outstanding characteristics as the above can be given to a constituent, and it can be the most desirable target for dealing in the improvement constituent of the mechanical property of a fluororesin, load deflection temperature, dimensional stability, and moldability, and a thermoplastic elastomer composition. As liquid crystal polyester used for this invention, for example Aromatic dicarboxylic acid, The liquid crystal copoly ester by which ***** component ***** of the ** is carried out from one sort of one sort of alicyclic dicarboxylic acid or two sorts or more, aromatic series diol, alicyclic diol, and aliphatic series diol or two sorts or more, one sort of aromatic hydroxycarboxylic acid, or

two sorts or more is raised. As typical combination, for example Para hydroxybenzoic acid, biphenyl diol, What makes terephthalic acid a principal component (for example, Eko Knoll E2000 by Sumitomo Chemical Co., Ltd., E6000, E7000, Xydar RC/FC400 made from Nippon Oil Chemistry, 300, Polyplastics Vectra C series) UENO made from Ueno Pharmaceuticals LCP2000, Idemitsu LCP300 made from Idemitsu Petrochemistry, what makes a principal component Para hydroxybenzoic acid and 6-hydroxy naphthoic acid (for example, ICI Japan VICTREX [] -- [SRP and J) UENO made from Ueno Pharmaceuticals LCP1000, Polyplastics Vectra A series and Mitsubishi Kasei Corp. Idemitsu LCP300 of the nova curate E324 of **, and the product made from Idemitsu Petrochemistry, rod run LC-5000 by Unitika, Ltd., Para hydroxybenzoic acid, terephthalic acid, What (for example, Idemitsu LCP100 of the nova curate E310 by Mitsubishi Kasei Corp. and the product made from Idemitsu Petrochemistry, rod run LC-3000 by Unitika, Ltd., X7G by Eastman Kodak Co.) makes aliphatic series diol a principal component is raised.

Especially when dealing in a thermoplastic elastomer composition by blending functional group content fluorine-containing elastomer and these liquid crystal polyester of this invention, the heat-resisting property of functional group content fluorine-containing elastomer is taken into consideration. What makes a principal component the thing which makes a principal component Para hydroxybenzoic acid with comparatively low melting temperature and 6-hydroxy naphthoic acid or Para hydroxybenzoic acid, terephthalic acid, and aliphatic series diol is desirable.

The mechanical property of fluorine-containing resin of the above among the fluorine-containing thermoplastics constituents containing aromatic polyester or polycarbonate of this invention obtained as mentioned above, [the constituent which improved load deflection temperature, dimensional stability, and moldability] In addition to it, it doubles and has the outstanding heat-resisting property of fluorine-containing resin original, chemical resistance, and an electrical property. As a result, electricity, electronic parts which need dimensional stability, a heat-resisting property, and an electrical property. For example, a connector, a chip, a carrier, a socket, a printed-circuit board, Wire covering material, the semiconductor related article which needs chemical resistance especially moldability, the large-sized wafer basket which was insufficient as for hardness and was [the fluororesin simple substance] difficult. Or it can become the parts of the circumference of the machine relation, for example, the fuel for cars, which needs a valve, chemical pump parts, a heat-resisting property, sliding nature, etc., a gear, an axle hole, etc. with a useful material especially.

[moreover, the thermoplastic elastomer composition which consists of a hydroxy group or carboxyl ester group content fluorine-containing elastomer, aforementioned aromatic polyester, or aforementioned polycarbonate] It is the constituent with which the portion of the aromatic polyester which gives the flowability in high temperature, or polycarbonate, and the portion of the fluorine-containing elastomer which can give rubber elasticity carried out the chemical bond to the constituent through the functional group of fluorine-containing elastomer, and the fluorine-containing elastomer component formed the continuous phase. Compared with the thermoplastic elastomer composition whose thermoplastics obtained by the constituent of this invention carrying out dynamic vulcanization of the fluorine-containing elastomer to the inside of conventional thermoplastics to whether it carried out is a continuous phase, it excels in a heat-resisting

property and chemical resistance. Moreover, since it is the constituent obtained only by carrying out a melting blend, without using a vulcanizing agent and an additive, the chemical-resistant fall by these impurities and contamination by elution can be prevented. Moreover, naturally the moldability by injection molding as a thermoplastic elastomer etc. and recycling efficiency are in a peach.

[therefore, the thermoplastic elastomer composition of this invention] Medical Science Division and the biochemistry fields, such as an inner tube, a vial plug, a gasket, and a syringe, an inner tube, Electricity and the electronic fields, such as the semiconductor industrial fields, such as O ring and seal material, heat-resistant wire covering material, and seal material, The food-stuff-industry fields, such as a hose and seal material, a fuel system hose, an inner tube, a gasket, It is a material useful for uses, such as the building-industries fields, such as the chemical industry fields, such as the automobile related fields, such as uniform SHOINDO boots and rack and pinion boots, a resisting pressure hose, diaphragm, packing, a gasket, and a hose, and a sealing material.

In the range in which the resin composition thing of this invention furthermore does not spoil the effect For example, glass fiber, carbon fiber, an aramid fiber, a graphite whisker, A potassium titanate whisker, a basic magnesium sulfate whisker, A magnesium whisker, a boric acid magnesium whisker, a calcium carbonate whisker, A calcium sulfate whisker, a zinc oxide whisker, a boric acid aluminium whisker, An alumina whisker, a silicon carbide whisker, a silicon nitride whisker, a WORASU night, Fibrous strengthening agents, such as zonolite, sepiolite, gypsum-fibrosus fiber, and slag fiber, Carbon powder, graphite powder, calcium carbonate powder, a talc, mica, Inorganic or organic bulking agents usually used, such as heat resistant resin, such as inorganic bulking agents, such as clay and a glass bead, and polyimide, the solid lubricant and other colorants still like molybdenum disulfide, and a flame retarder, may be included, and the loadings are usual [of the whole constituent / 1 to 30% of]. At this time, when the unreacted functional group contained in the resin composition thing of this invention exists, these restoration effects may improve further.

Although a mixing mill, a Banbury mixer, a Brabender mixer, an extruder, etc. are raised as equipment which is used by this invention and which carries out melting mixing It is the point which kneading power of an extruder is larger and improvement in dispersibility can expect further especially at the time of a blend, and the productivity at the time of manufacture of a constituent is desirable at a good point. Although what has a single axis or the screw of two or more axes can be used as an extruder, it is desirable to use especially a twin screw extruder at the point which the good constituent of dispersibility is ***** since kneading power is larger, and can control kneading power freely.

Brief explanation of the drawings Drawing 1 is the figure which measured the surface tension in work examples 11 and 12.

Drawing 2 is the scanning type electron microscope photograph of the cutting plane of the mold goods obtained in the work example 55.

Drawing 3 is the scanning type electron microscope photograph of the cutting plane of the mold goods obtained in the work example 56.

Drawing 4 is the scanning type electron microscope photograph of the cutting plane of the mold goods obtained by the comparative example 10.

Drawing 5 is the scanning type electron microscope photograph of the cutting plane of

the mold goods obtained by the comparative example 11.

Drawing 6 is a stress-strain curve in the tension test of the mold goods obtained by work examples 66-68 and a comparative example 22.

The best form for inventing Although the example of manufacture of the thermoplastics constituent which used fluorine-containing olefin of this invention, the synthetic example of a fluorine polymer, and the fluorine polymer is explained still more concretely below based on a work example, this inventions are not these things limited to seeing.

I. Example about functional group content fluorine-containing monomer.

The following simplified characters and a sign are used in the following examples.

R-11: Trichlorofluoromethane NMR: Nuclear magnetic resonance spectrum IR: Infrared absorption spectrum MS: Mass spectrum.

Example 1 of reference 2 and 2-difluoro 3-iodine PUROPIONIRUFURUORAIDO (ICH2CF2COF)

3l. 825g of sodium iodide was dissolved completely, putting in tetraglyme 1500ml into a 4 Thu mouth flask, and agitating at a room temperature. Then, 2, 2, 3, and 3-tetrafluoro oxetane 650g was slowly dropped [water] for reaction temperature at the condensor in 30-40 degrees C with through, and dropping was ended in 45 minutes.

The mark compound 2 and 2-difluoro 3-iodine PUROPIONIRUFURUORAIDO 1050g were collected from the reaction mixture by distilling at 38-40 degrees C under the reduced pressure of 30mmHg.

95-96 degrees C of boiling points.

Example 2 of reference Perfluoro (6 and 6-dihydro 6-iodine 2-trifluoromethyl 3-OKISA hexanoic acid) methyl (ICH2CF2CF2OC-(CF3) FCOOCH3) Synthesis 2l. In a 4 Thu mouth flask, caesium full ORAIDO 43g, 2 and 2-difluoro 3-iodine PUROPIONIRUFURUORAIDO 400g obtained in the example 1 of reference in tetraglyme 6ml was put in, and the internal temperature was 10 degrees C under churning. It continued, and after making hexafluoro propylene oxide flow from a cylinder for 21 hours at the velocity which flows back with a dry ice condensor, methanol 300ml was added, cooling by iced water. After washing a resultant several times, a mark compound and perfluoro (6 and 6-dihydro 6-iodine 2-trifluoromethyl 3-*****- hexanoic acid) methyl were obtained by distillation. The yield of 250g, 116-117 degrees C (60mmHg) of boiling points.

example 3 of reference Perfluoro (9 and 9-dihydro 9-iodine 2, 5-screw trifluoromethyl 3, 6-dioxa nonoic acid) methyl (ICH2CF2CF2OC-(CF3) FCF2OC-(CF3) FCOOCH3) Synthesis 2l. 2 and 2-difluoro 3-iodine PUROPIONIRUFURUORAIDO 600g obtained in caesium full ORAIDO 60g and tetraglyme 10ml and the example 1 of reference was put into the 4 Thu mouth flask, and the internal temperature was 10 degrees C under churning. It continued, and after making hexafluoro propylene oxide flow from a cylinder for 30 hours at the velocity which flows back with a dry ice condensor, methanol 500ml was added, cooling by iced water. After washing a resultant several times, a mark compound and perfluoro (9 and 9-dihydro 9-iodine 2, 5-screw trifluoromethyl 3, 6-dioxa nonoic acid) methyl were obtained by distillation. The yield of 116g, 100-101 degrees C (15mmHg) of boiling points.

example 4 of reference Perfluoro (12 and 12-dihydro 12-iodine 2 and 5, 8-tris trifluoromethyl 3 and 6, 9-trioxadodecanoic acid) methyl (synthetic [ICH2CF2CF2OC-(CF3) FCF2OC-(CF3) FCF2OC-(CF3) FCOOCH3]) Mark compound

perfluoro (12, 12, and dihydro 12-iodine 2 and 5, 8-tris trifluoromethyl 3 and 6, 9-trioxadodecanoic acid) methyl was obtained by distillation after washing the resultant acquired like the example 3 of reference. The yield of 85g, 105-106 degrees C (2mmHg) of boiling points.

Work example 1 Perfluoro (6 and 6-dihydro 2-trifluoromethyl 3-*****- 5-hexene acid) methyl (synthesis of $\text{CH}_2=\text{CFCF}_2\text{OC}(\text{CF}_3)\text{FCOOCH}_3$)

1l. with an agitator, a condensator, and a dropping funnel Methanol 500ml and 84.6g of zinc dust were put into the 4 Thu mouth flask, and the internal temperature was 60-65 degrees C. Perfluoro obtained in the example 2 of reference while agitating (6 and 6-dihydro 6-iodine 2-trifluoromethyl 3-OKISA hexanoic acid)

Methyl 270g was dropped over about 1 hour from the dropping funnel. It cooled to the room temperature after 1-hour churning at further 65-68 degrees C.

It released to 1l. of 1N-hydrochloric acid, after filtering the reaction mixture and separating superfluous zinc. After gentle placement, the organic layer was separated, and it washed, and dried, and mark compound perfluoro (6 and 6-dihydro 2-trifluoromethyl 3-*****- 5 hexene acid) methyl was obtained by distilling. The yield of 171.9g, 72-73 degrees C (95mmHg) of boiling points.

1 H-NMR:delta (ppm) (inch CDCl_3), 5.55-5.38 (2H, m), 4.06 (3H, s.br.).

19 F-NMR:delta (ppm) (inch CDCl_3 , R-11 internal standard), -70.8--71.5 (1F, m), -77.5--78.1 (1F, m), -82.3 (3F, s.br)

-124.2--124.5 (1F, m), -131.3--131.4 (1F, m).

IR(cm-1): 1787 (nuc=o), 1695 (nuc=c).

MS(m/e): 270 (P), 159 (C-(CF_3) FCOOCH_3), 95 ($\text{CH}_2=\text{CFCF}_2$), 69 (CF_3), 59 (COOCH_3), 15 (CH_3).

Work example 2 Perfluoro (6 and 6-dihydro 2-trifluoromethyl 3-*****- 5-hexene acid)

Synthesis of ($\text{CH}_2=\text{CFCF}_2\text{OC}-(\text{CF}_3)\text{FCOOH}$) 500ml with an agitator, a condensator, and a dropping funnel Put 17.1g of sodium hydroxide, and methanol 300ml into the 4 Thu mouth flask, it was made to dissolve completely, and the internal temperature was maintained at the room temperature. The perfluoro (6 and 6-dihydro 2-trifluoromethyl 3-*****- 5-hexanoic acid) methyl 100g obtained in the work example 1 was dropped over about 30 minutes from the dropping funnel, agitating. Furthermore, it released to 1l. of 2N-hydrochloric acid after churning at the room temperature for 1 hour. Mark compound perfluoro (6 and 6-dihydro 2-trifluoromethyl 3-*****- 5-hexanoic acid) was obtained by separating and washing it, drying it and distilling an organic layer after gentle placement. The yield of 50.5g, 81-82 degrees C (20mmHg) of boiling points.

1 H-NMR:delta (ppm) (inch CDCl_3), 11.5 (1H, s.br.)

5.50-5.37 (2H, m).

19 F-NMR:delta (ppm) (inch CDCl_3 , R-11 internal standard), -70.5--71.3 (1F, m), -77.2--77.8 (1F, m), -82.4 (3F, m), -124.1--124.4 (1F, m), -131.3--131.5 (1F, m).

IR(cm-1): 3511(nu un-meeting OH) 2655-3300 (nu meeting OH), 1771 (nuc=o), 1695 (nuc=c).

MS(m/e): 256 (P), 145 (C-(CF_3) FCOOH), 95 ($\text{CH}_2=\text{CFCF}_2$), 69 (CF_3), 45 (COOH).

Work example 3 Perfluoro (1, 1, 6, and 6-tetrahydro 2-trifluoromethyl 3-*****- 5-hexenol)

Synthesis of ($\text{CH}_2=\text{CFCF}_2\text{OC}-(\text{CF}_3)\text{FCH}_2\text{OH}$) Agitator, Perfluoro (6 and 6-dihydro 6-iodine 2-trifluoromethyl 3-OKISA hexanoic acid) methyl 416g and ethanol 500ml

obtained in the example 2 of reference was added to the 3l. 4 Thu mouth flask with a condenser and a dropping funnel, and the internal temperature was kept at 0-5 degrees C. The solution in which ethanol 600ml was made to dissolve the sodium boron hydride (NaBH₄) 26.5g was dropped over about 4 hours from the dropping funnel, agitating. The internal temperature was kept at 0-10 degrees C in the meantime.

Furthermore, the reaction mixture was slowly released to 3l. of 1N-hydrochloric acid after 2-hour churning at 0-10 degrees C. It is perfluoro (1, 1, 6, and 6-tetrahydro 6-iodine 2-trifluoromethyl 3-*****- hexanol) by separating liquids, washing and drying and distilling an organic layer after gentle placement.

(ICH₂CF₂CF₂OC-(CF₃) FCH₂OH) 281g was obtained. 75-77 degrees C (5mmHg) of boiling points.

59.2g of zinc dust and methanol 200ml was put into the 500ml 4 Thu mouth flask which offered the agitator, the condenser, and the dropping funnel, and the internal temperature was kept at 60-65 degrees C. Agitating, 271g of the aforementioned higher alcohol prepared by reduction was dropped over about 1 hour, and it heated at further 60-65 degrees C after the end of dropping for 1 hour. The reaction mixture was processed by the same method as a work example 1, and mark compound perfluoro (1, 1, 6, and 6-tetrahydro 2-trifluoromethyl 3-*****- 5-hexenol) was obtained. The yield of 103g, 76-77 degrees C (95mmHg) of boiling points.

1 H-NMR:delta (ppm) (inch CDCl₃), 5.47-5.30 (2H, m), 5.15 (1H, t, J = 6.3Hz), 4.28-4.19 (2H, m).

19 F-NMR:delta (ppm) (inch CDCl₃, R-11 internal standard), -71.7--72.3 (1F, m), -73.1--73.7 (1F, m), -81.5 (3F, s, br)

-123.2--123.5 (1F, m), -134.3--134.5 (1F, m).

IR(cm-1): 3631 (nu un-meeting OH), 3411 (nu meeting OH), 1695 (nuc=c).

MS(m/e): 242 (P), 131 (C-(CF₃) FCH₂OH), 95 (CH₂=CF₂CF₂), 69 (CF₃), 31 (CH₂OH).

Work example 4 Perfluoro (9 and 9-dihydro 2, 5-screw trifluoromethyl 3, 6-dioxa 8-nonene acid) methyl (CH₂=CF₂CF₂OC-(CF₃) FCF₂OC(CF₃) FCOOCH₃) Synthesis Agitator, [put 1l. of methanol, and 127g of zinc dust into a 2l. 4 Thu mouth flask with a condenser and a dropping funnel, and / 63-68 degrees C / with the same method as a work example 1] The perfluoro (9 and 9-dihydro 9-iodine 2, 5-screw trifluoromethyl 3, 6-dioxa nonoic acid) methyl 873g obtained in the example 3 of reference was made to react. The mixture after a reaction was processed by the same method as a work example 1, and mark compound perfluoro (9 and 9-dihydro 2, 5-screw trifluoromethyl 3, 6-dioxa 8-nonene acid) methyl was obtained. The yield of 482g, 70-71 degrees C (16mmHg) of boiling points.

1 H-NMR:delta (ppm) (inch CDCl₃), 5.32-5.16 (2H, m, JHF = 47.6 or 16.8Hz), 3.49 (3H, s, br).

19 F-NMR:delta (ppm) (inch CDCl₃, R-11 internal standard), - 73.9--74.4 (2F, m), -79.1--80.0 (1F, m), - 80.6 (3F, m), -83.1 (3F, m), -86.3--86.8 (1F, m), -123.2--123.6 (1F, m, JHF=47.6, 16.8Hz), -132.3-132.7 (1F, m), 146.3--146.8 (1F, m).

IR(cm-1): 1790 (nuc=O), 1695 (nuc=c).

MS(m/e): 436 (P), 325 (P-CF₂=CF₂CF₂O), 159 (C-(CF₃) FCOOCH₃), 95 (CH₂=CF₂CF₂), 69 (CF₃), 59 (COOCH₃), 15 (CH₃).

Work example 5 Perfluoro (9 and 9-dihydro 2, 5-screw trifluoromethyl 3, 6-dioxa 8-nonene acid)

Synthesis of (CH₂=CFCF₂OC-(CF₃) FCF₂OC-(CF₃) FCOOH) 43g of sodium hydroxide and methanol 700ml was put into the 2l. 4 Thu mouth flask with an agitator, a condensator, and a dropping funnel, and it was made to dissolve in it completely. The hydrolysis reaction of the perfluoro (9 and 9-dihydro 2, 5-screw trifluoromethyl 3, 6-dioxa 8-nonenone acid) methyl 403g of a work example 4 was carried out by the method as a work example 2 that next it is the same. It processed by the same method as a work example 2, and a mark compound and perfluoro (9 and 9-dihydro 2, 5-screw trifluoromethyl 3, 6-dioxa 8-nonenone acid) were obtained. The yield of 332g, 79-80 degrees C (0.12mmHg) of boiling points.

¹H-NMR:delta (ppm) (inch CDCl₃), 12.5 (1H, s.br.), 5.60-5.30 (2H, m).

¹⁹F-NMR:delta (ppm) (inch CDCl₃, R-11 internal standard), - 72.7--73.0 (2F, m), -78.2--79.2 (1F, m), -79.7 (3F, m), -82.3 (3F, m), -84.1--85.0 (1F, m), -124.1--124.4 (1F, m) -131.1--131.3 (1F, m), -145.3-145.7 (1F, m).

IR(cm-1): 3520 (nu un-meeting OH), 2650-3300 (nu meeting OH), 1772 (nuc=o), 1694 (nuc=c).

MS(m/e): 442 (P), 311 (C-(CF₃) FCH₂C(CF₃) FCOOH), 95 (CH₂=CFCF₂), 69 (CF₃), 45 (COOH).

Work example 6 Perfluoro (1, 1, 9, and 9-tetrahydro 2, 5-screw trifluoromethyl 3, 6-dioxa 8-nonenol)

Synthesis of (CH₂=CFCF₂OC-(CF₃) FCF₂OC-(CF₃) FCH₂OH) Were obtained in the example 3 of reference. Using the perfluoro (9 and 9-dihydro 9-iodine 2, 5-screw trifluoromethyl 3, 6-dioxa nonoic acid) methyl 582g, by a sodium boron hydride (NaBH₄) like a work example 3 A reduction reaction, Isolation operation is performed and it is perfluoro (1, 1, 9, and 9-tetrahydro 9-iodine 2, 5-screw trifluoromethyl 3, 6-dioxa nonanol).

(ICH₂CF₂CF₂OC-(CF₃) FCF₂OC-(CF₃) FCH₂OH) 365g was obtained. 65-66 degrees C (0.4mmHg) of boiling points.

Next, deIF reaction and isolation operation are performed with 46.5g of zinc dust by the same method as a work example 3 using 305g of higher alcohol prepared by reduction obtained above. Mark compound perfluoro (1, 1, 9, and 9-tetrahydro 2, 5-screw trifluoromethyl 3, 6-dioxa 8-nonenol) was obtained. The yield of 351.2g, 77-78 degrees C (14mmHg) of boiling points.

¹H-NMR:delta (ppm) (inch CDCl₃), 5.31-5.12 (2H, m), 4.19-4.12 (2H, m), 2.80 (1H, m).

¹⁹F-NMR:delta (ppm) (inch CDCl₃, R-11 internal standard), - 74.3--74.6 (2F, m), -80.2--80.7 (1F, m), - 81.0 (3F, m), -82.1--82.9 (1F, m), 83.3 (3F, m), -123.6-124.1 (1F, m), -137.1--137.4 (1F, m), 146.3--146.5 (1F, m).

IR(cm-1): 3630 (nu un-meeting OH), 3405 (nu meeting OH), 1699 (nuc=c).

MS(m/e): 408 (P), 261 (CH₂=CFCF₂OC-(CF₃) CF)

131 (C-(CF₃) FCH₂OH), 95 (CH₂=CFCF₂), 69 (CF₃), 31 (CH₂OH).

work example 7 perfluoro (12 and 12-dihydro 2 and 5, 8-tris trifluoromethyl 3 and 6, 9-trioxa 11-DODEKENE acid) methyl Synthesis of CH₂=CFCF₂OC-(CF₃) FCF₂OC-(CF₃) FCF₂OC-(CF₃) FCOOCH₃ [the perfluoro (12 and 12-dihydro 12-iodine 2 and 5, 8-tris trifluoromethyl 3 and 6, 9-trioxa dodecanoic acid) methyl 187g and 21.2g of zinc dust which were obtained by the method of the example 4 of reference / with the same method as a work example 2] Mark compound perfluoro (12 and 12-dihydro 2 and 5, 8-tris

trifluoromethyl 3 and 6, 9-trioxa 11-DODEKEN acid) methyl was obtained by performing a delf reaction into methanol and performing isolation operation. The yield of 96.3g, 117-118 degrees C (20mmHg) of boiling points.

¹H-NMR:delta (ppm) (inch CDCl₃), 5.55 (1H, dd, J= 15.6, 4.7Hz), 5.46 (1H, dd, J= 42.9, 4.7Hz), 4.12 (3H, S).

¹⁹F-NMR:delta (ppm) (inch CDCl₃, R-11 internal standard), - 72.8--73.3 (2F, m), -78.4--79.4 (2F, m), - 79.6--80.1 (6F, m), -82.2--82.4 (3F, m), -84.2--85.3 (2F, m), -124.2-124.7 (1F, m), -131.0--131.3 (1F, m), -145.0--145.5 (2F, m).

IR(cm-1): 1791 (nuc=o), 1696 (nuc=c).

MS(m/e): 602 (P), 491 (P-CH₂=CFCF₂), 427 (P-OC-(CF₃) FCOOCH₃), 325 (C-(CF₃) FCF₂OC-(CF₃) FCOOCH₃), 261 (CH₂=CFCF₂OC-(CF₃) FCF₂)

159 (C-(CF₃) FCOOCH₃), 95 (CH₂=CFCF₂), 69 (CF₃)

59 (COOCH₃), 15 (CH₃).

work example 8 synthesis of perfluoro (12 and 12-dihydro 2 and 5, 8-tris trifluoromethyl 3 and 6, 9-trioxa 11-DODEKEN acid) (CH₂=CFCF₂OC-(CF₃) FCF₂OC-(CF₃)

FCF₂OC-(CF₃) FCOOH) Synthesis [with the same method as a work example 2] [methanol solution of 7.6g of sodium hydroxide] The perfluoro which used and was obtained in the work example 7 (12 and 12-dihydro 2 and 5, 8-tris trifluoromethyl 3 and 6, 9-trioxa DODEKEN acid) performing a Methyl [90.3g] hydrolysis reaction and isolation operation -- mark compound perfluoro (12 and 12-dihydro 2 and 5 and 8-tris trifluoromethyl 3 --) The 6 and 9-trioxa 11-DODEKEN acid was obtained. The yield of 59.0g, 110-112 degrees C (0.15mmHg) of boiling points.

¹H-NMR:delta (ppm) 11.72 (1H, br.s.), 5.55-5.30 (2H, m).

¹⁹F-NMR:delta (ppm) (inch CDCl₃, R-11 internal standard), - 72.8--73.4 (2F, m), -78.5--79.5 (2F, m), - 79.6--80.5 (6F, m), -82.4--82.7 (3F, m), -83.9--85.6 (2F, m), -124.1-124.5 (1F, m), -130.8--131.4 (1F, m), 145.1--145.6 (2F, m).

IR(cm-1): 3533 (nu un-meeting OH), 2650-3300 (nu meeting OH), 1779 (nuc=o), 1696 (nuc=c).

MS(m/e): 588 (P), 427 (P-OC-(CF₃) FCOOH), 261 (CH₂=CFCF₂OC-(CF₃) FCF₂-), 95 (CH₂=CFCF₂), 69 (CF₃), 45 (COOH).

Work example 9 Perfluoro (9 and 9-dihydro 2, 5-screw trifluoromethyl 3, 6-dioxa 8-nonene acid) ammonium (CH₂=CFCF₂OC-(CF₃) FCF₂OC-(CF₃) FCOONH₄)

***** [the small quantity of the perfluoro (9 and 9-dihydro 2, 5-screw trifluoromethyl 3, 6-dioxa 8-nonene acid) obtained in the work example 5] When the number of equivalent of the base required to make it dissolve in ethanol, and for 0.1 N-KOH / ethanol standard solution perform neutralization titration using potentiometric titration equipment, and neutralize per this 1g of carboxylic acid was measured, it was 2.42x10 - 3Eq.

[19.2g of the same carboxylic acid compounds as the above / measuring concentration by titration] next It dissolves in 46.5ml of 1.0N-aqueous ammonia, and it is neutralized, it shall move to a 200 moreml volumetric flask, water shall be added, the whole quantity shall be 200ml, and they are a mark compound and perfluoro (9 and 9-dihydro 2, 5-screw trifluoromethyl 3, 6-dioxa 8-nonene acid).

The 10% (wt/Vol) aqueous solution of ammonium was obtained.

Suction drying was repeated [this solution] for the part at 80 degrees C, and the white solid was obtained.

1 H-NMR:delta (ppm) (inch D2O), 5.41-5.14 (2H, m), 4.96-4.72 (4H, dr.s.).

19 F-NMR:delta (ppm) (inch D2O, R-11 internal standard), - 73.9--74.4 (2F, m), -80.7--81.0 (3F, m), - 81.0--82.6 (2F, m), -83.1--83.3 (3F, m), -125.2--125.5 (1F, m), -126.7-127.0 (1F, m), -146.3--146.8 (1F, m).

IR(cm-1, the KBr method): 3590-2700 (nuN-H), 1688 (nuc=c), 1664 (nuc=o).

work example 10 Perfluoro (12 and 12-dihydro 2 and 5, 8-tris trifluoromethyl 3 and 6, 9-trioxa 11-DODEKEN acid) ammonium ($\text{CH}_2=\text{CFCF}_2\text{OC}-(\text{CF}_3)\text{FCF}_2\text{OC}-(\text{CF}_3)$

$\text{FCF}_2\text{OC}-(\text{CF}_3)\text{FCOONH}_4$) Synthesis Mix [31.0ml of 1N-aqueous ammonia, and] the perfluoro (12 and 12-dihydro 2 and 5, 8-tris trifluoromethyl 3 and 6, 9-trioxa 11-DODEKEN acid) 19.4g compounded in the work example 8 by the same method as a work example 9, and it neutralizes. The whole was diluted to 200ml with water, and 10% (wt/Vol) of solution of mark compound perfluoro (12 and 12-dihydro 2 and 5, 8-tris trifluoromethyl 3 and 6, 9-trioxa 11-DODEKEN acid) ammonium was obtained.

Suction drying was repeated at 80 degrees C for a part of this solution, and the white solid was obtained.

1 H-NMR:delta (ppm) (inch D2O), 5.26-5.00 (2H, m), 4.9-4.74 (4H, br.s.).

19 F-NMR:delta (ppm) (inch D2O, R-11 internal standard)-79.5--86.5 (4F, m), - 81.0--82.5 (6F, m), -83.0--84.0 (3F, m), -124.5--126.0 (1F, m), -127.0--128.0 (1F, m), -146.8--148.0 (2F, m).

IR(cm-1): 3560-2730 (nuN-H), 1694 (nuc=c), 1661 (nuc=o).

Work example 11 Use as an emulsifier of perfluoro (9 and 9-dihydro 2, 5-screw trifluoromethyl 3, 6-dioxa 8-nonene acid) ammonium (measurement of critical micelle concentration (henceforth cmc))

The aqueous solution from which it dilutes with water further and concentration differs was prepared using the 10% aqueous solution of said ammonium salt obtained in the work example 9, and each surface tension was measured. A result is shown in [drawing 1](#) .

When cmc was read from [drawing 1](#) , it was 59.2 mmol/a liter.

Work example 12 Use as an emulsifier of perfluoro (12 and 12-dihydro 2 and 5, 8-tris trifluoromethyl 3 and 6, 9-trioxa 11-DODEKEN acid) ammonium (measurement of cmc)

Surface tension was measured like the work example 11 except having used the ammonium salt compounded in the work example 10 instead of said ammonium salt obtained in the work example 9.

A result is shown in [drawing 1](#) .

cmc was 8.3 mmol(s)/a liter from [drawing 1](#) .

Each ammonium salt obtained in work examples 9 and 10 from [drawing 1](#) has good surface activity capability, and can use it as a reactant emulsifier.

Work example 13 2, 3, 3, 5, 6, 6, 8-heptafluoro 4 and 7, 10-trioxa 5, 8-screw trifluoromethyl 12, 13-epoxy tridecane 1-EN

$(\text{CH}_2 = \text{CFCF}_2\text{OC} - (\text{CF}_3)\text{FCF}_2\text{OC} - (\text{CF}_3)\text{FCH}_2\text{OCH}_2\text{CHCH}_2)$ の合成



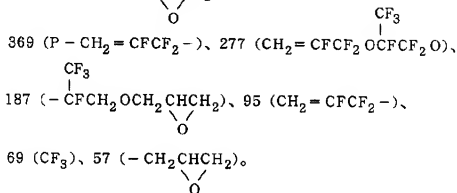
The perfluoro (1, 1, 9, and 9-tetrahydro 2, 5-screw trifluoromethyl 3, 6-dioxa 8-nonene) 62.6g obtained by the 300ml 4 Thu mouth flask equipped with the agitator and the condenser in the work example 6, Epichlorohydrin 70.6g was added and it heated at 80 degrees C. 7.8g of sodium hydroxide was added over about 30 minutes there in 3 steps. The internal temperature was kept at 80-90 degrees C in the meantime. After agitating for

30 minutes at 80 more degrees C, it cooled to the room temperature.

[release a reaction mixture to 500ml of pure water, after gentle placement, separate an organic layer, wash, dry, and] by distilling The mark compounds 2, 3, 3, 5, 6, and 6, 8-heptafluoro 4 and 7, 10-trioxa 5, 8-screw trifluoromethyl 12, and 13-epoxy tridecane 1-EN were obtained. The yield of 46.8g, 78-80 degrees C (0.2mmHg) of boiling points. 1 H-NMR:delta (ppm) (inch CDCl3), 5.63-5.37 (2H, m), 4.40-4.19 (2H, m), 4.05-3.95 (1H, m), 3.59-3.48 (1H, m), 3.20-3.09 (1H, m), 2.81-2.72 (1H, m), 2.64-2.54 (1H, m). 19 F-NMR:delta (ppm) (inch CDCl3, R-11 internal standard), -72.6--73.0 (2F, m), -79.4--79.6 (3F, m), -79.1--80.2 (1F, m), -80.7--81.6 (1F, m), -82.0--82.2 (3F, m), -124.0-124.4 (1F, m), -132.8--133.2 (1F, m), 145.1--145.6 (1F, m)

IR(cm-1): 1695 (nuc=c).

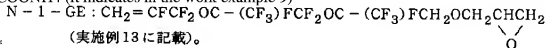
MS (m/e): 464 (P), 421 (P - CHCH₂),



II. the example about a functional group content fluorine polymer.

The following are used as a cable address of the functional group content fluorine-containing monomer (A) used for the polymer of this invention, and the other monomers (B) which carry out copolymerization.

N-0-OH:CH₂=CFCF₂OC-(CF₃) FCH₂OH (it indicates in the work example 3), N-1-OH:CH₂=CFCF₂OC-(CF₃) FCF₂OC-(CF₃) FCH₂OH (it indicates in the work example 6), N-0-COOH:CH₂=CFCF₂OC-(CF₃) FCOOH (it indicates in the work example 2), N-1-COOH:CH₂=CFCF₂OC-(CF₃) FCF₂OC-(CF₃) FCOOH (it indicates in the work example 5), N-2-COOH:CH₂=CFCF₂O-[C-(CF₃) FCF₂O]₂-OC-(CF₃) FCOOH (it indicates in the work example 8), N-1-COONH₄:CH₂=CFCF₂OC-(CF₃) FCF₂OC-(CF₃) FCOONH₄ (it indicates in the work example 9)



**

(実施例 13 に記載)。

TFE : Tetrafluoroethylene, VdF : Vinylidene fluoride, HFP: Hexafluoropropylene CTFE: Chlorotrifluoroethylene PPVE: Perfluoro (propyl vinyl ether) PMVE: Perfluoro (methyl vinyl ether) E: Ethylene.

Moreover, in the following examples, the following simplified characters, a sign, and language are used.

As a catalyst IPP: Diisopropyl peroxi dicarbonate NPP: Di-n-propyl peroxi dicarbonate

APS: Ammonium persulfate.

As an emulsifier PFOA: Perfluoro octanoic acid ammonium (C7F15COONH4)

As a solvent R-141b: 1 and 1-dichloro 1-fluoro ethane, R-113: 1, 1, 2-bird chloro 1 and 2, 2-trifluoro ethane R-114:1, 2-dichloro 1, 1, and 2, 2-tetrafluoro ethane THF:

Tetrahydrofuran DMF: Dimethylformamide.

In measurement analysis relations DSC : A differential scanning calorimetry, Tg : Glass transition temperature, Tm : A fusing point, Td : Pyrolysis temperature (it was considered as temperature when weight decreases 1% in the air, and temperature in case weight decreases 1% by the heating rate of 10 degrees C / min among the air was measured using the Shimadzu Corp. make thermal-analysis equipment DT-30 type), GPC molecular weight : The polystyrene conversion molecular weight by gel permeation chromatographic analysis (based on a THF solvent or a DMF solvent), Mn : A number average molecular weight, Mw: Weight average molecular weight Flow value: The volume (ml/sec) of the copolymer which flows out of a nozzle into unit time is measured, and let it be a flow value, after carrying out for preheating 5 minutes using a nozzle 2mm in diameter, and 8mm in length using a quantity-sized type flow tester.

Work example 14 Copolymerization of perfluoro (1, 1, 9, and 9-tetrahydro 2, 5-screw trifluoromethyl 3, 6-dioxa 8-nonenol) and tetrafluoroethylene Valve, [the 250ml autoclave equipped with the pressure gauge and the thermometer] The perfluoro (1, 1, 9, and 9-tetrahydro 2, 5-screw trifluoromethyl 3, 6-dioxa 8-nonenol) 16.3g and 1 obtained in the work example 6 as shown in Table 1, 1-dichloro 1-fluoro ethane (R-141b), 60g, Diisopropyl peroxy dicarbonate (IPP) 0.10g was put in, and after cooling with dry ice / methanol liquid, nitrogen replaced the inside of a system enough. subsequently, Tetrafluoroethylene (TFE) 6.3g is taught, and it carried out by having obtained with ** for 20 hours, and was made to react at 45 degrees C from a valve

表 1

反応条件	実施例番号	14	15	16	17	18
官能基含有単置体 (A)		N-1-OH	N-1-OH	N-1-OH	N-0-OH	N-1-COOH
仕込み量 (g)		16.3	2.4	20.4	1.1	2.6
単置体 (B)	T F E (g)	6.3	-	-	-	-
仕込み量	V d F (g)	-	4.5	4.5	6.9	9.4
開始剤		IPP	IPP	IPP	IPP	IPP
仕込み量 (g)		0.10	0.08	0.13	0.12	0.16
溶 剤		R-141b	R-141b	R-141b	R-113	R-113
仕込み量 (g)		60	60	60	40	40
反応温度 (°C)		45	45	45	45	45
反応時間 (hr)		20	20	20	17	19

Gage pressure fell from 4.3kg/cm²G to 2.1kg/cm²G before a reaction with advance of the reaction. After emitting an unreacted monomer, take out the depositing solid matter, made it dissolve in acetone, it was made to reprecipitate by hexane, and the copolymer was separated. Suction drying was performed until it became constant weight, and 4.1g of

copolymers were obtained.

The composition ratio of this copolymer was checked from ^1H -NMR and ^{19}F -NMR analysis, and existence of a functional group was checked from the infrared absorption spectrum.

Moreover, as for the molecular weight of the copolymer, glass transition temperature (T_g) measured [reduced property / of GPC measurement / polystyrene] pyrolysis temperature by thermogravimetric measurement from DSC. A result is shown in Table 2.

表 2

重 合 結 果		実施例番号	14	15	16	17	18
ポ リ マ ー 組 成	吸 量 (g)		4.1	4.5	4.5	7.3	15.8
	官能基含有単量体 (A)		N-1-OH	N-1-OH	N-1-OH	N-0-OH	N-1-COOH
	含有モル%		73.3	15.8	51.8	0.5	0.9
	単量体 (B)	T F E	26.7	-	-	-	-
D S C 測 定 (°C)	含有モル%	V d F	-	84.2	48.2	99.5	99.1
		T g	-1.1	-8.9	-8.1	-	-
1%熱分解温度 (°C)		T m	-	-	-	171.7	172
		T d	204.7	351	341	358	297
GPC分子重 $\times 10^4$ (THF系 ¹⁾ , DMF系 ²⁾)		M n	1.8 1)	1.8 1)	1.2 1)	7.1 2)	7.4 2)
		M w	3.0	2.9	2.4	12.4	14.8
I R 分析 (cm ⁻¹)	ν 非会合OH		3656	3645	3640	3622	3685
	ν 会合OH		3466	3440	3425	3455	~2800
	ν C = O		-	-	-	-	1770

Work examples 15-18 Copolymerization of a functional group content fluorine-containing monomer and vinylidene fluoride The monomer, initiator, and solvent (and the weight) of the work example 14 were changed into the monomer, initiator, and solvent (and the weight) which were indicated to Table 1, and also the copolymer was

obtained in the same procedure as a work example 14.

However, separation of the copolymer after the end of a reaction was the method same about work examples 15 and 16 as a work example 14, and about work examples 17 and 18, after swabbing in methanol by washing the obtained white powder, it was acquired by carrying out suction drying. Each of the yield in each copolymer, the copolymerization composition by NMR analysis, a thermal analysis (Tg, Tm, Td), and the measurement result of molecular weight is shown in Table 2.

Work example 19 Copolymerization of perfluoro (1, 1, 6, and 6-tetrahydro 2-trifluoromethyl 3-*****- 5-hexenol), and tetrafluoroethylene/ethylene Valve, The perfluoro (1, 1, 6, and 6-tetrahydro 2-trifluoromethyl 3-*****- 5-hexenol) 1.4g obtained in the work example 3 as shown in the 500ml auto crepe equipped with the pressure gauge and the thermometer in Table 3, 1, 1, 2-bird chloro 1 and 2, 2-trifluoro ethane (R-113) 100g, and diisopropyl peroxy G carbonate (IPP) 0.13g were put in, and after cooling with dry ice / methanol liquid, nitrogen replaced the inside of a system enough. subsequently, 30.3g of monomer mixtures of the molar ratio 80:20 of tetrafluoroethylene and ethylene which carried out mixed preparation in the cylinder beforehand are taught, and it carried out by having obtained with ** for 1.5 hours, and was made to react with the internal temperature of 45 degrees C from a valve

表 3

実施例番号		19	20	21	22	23	24	25	26
反応条件	官能基含有単量体 (A)	N-0-OH 仕込み量 (g)	N-1-OH 2.1	N-1-OH 2.1	N-1-COOH 2.2	N-1-OH 1.54	N-0-OH 1.64	N-1-OH 1.84	N-1-GE 2.86
	単量体 (B)	TFE	80	52	80	20	20	14	20
		混合モノ (モノルマ%)	-	-	-	80	60	74	60
		HFP	-	-	-	-	20	-	20
		CTFE	-	-	-	-	-	12	-
混合モノ/マ-仕込み量 (g)	E	20	20	48	20	-	-	-	-
	混合モノ/マ-仕込み量 (g)	30.3	33.8	23.8	33.5	17.8	33.6	16.3	34.6
開始剤	仕込み量 (g)	IPP	IPP	IPP	IPP	IPP	IPP	IPP	IPP
	仕込み量 (g)	0.13	0.13	0.13	0.14	0.10	0.18	0.11	0.16
溶媒	仕込み量 (g)	R-1113	R-1113	R-1113	R-1113	R-1113	R-1113	R-1113	R-1113
	仕込み量 (g)	100	100	100	100	100	100	100	100
反応温度 (°C)		45	45	45	45	45	45	45	45
反応時間 (hr)		1.5	4.0	5.0	2.0	20	17	20	5.0

Gage pressure fell with the reaction from 12.0 kgf/cm 2G to 7.5 kgf/cm 2G before a reaction.

The unreacted monomer was emitted, the depositing white powdered solid was taken out, after performing flush and acetone washing, suction drying was performed, and 15.6g of

copolymers were obtained.

The composition ratio of the obtained copolymer was checked from ^{19}F -NMR and a ultimate analysis, and existence of a functional group was checked from the infrared absorption spectrum.

Moreover, the flow value was measured for the fusing point of the copolymer by DSC using the quantity-ized type flow tester. A result is shown in Table 4.

表 4

重合結果		実施例番号								
ポリマ組成	収 量 (g)	19	20	21	22	23	24	25	26	
	官能基含有単量体 (A)	15.6	16.0	12.5	13.0	13.2	13.8	11.6	20.2	
	含有モル%	N-0-OH	N-1-OH	N-1-OH	N-1-COOH	N-1-OH	N-0-OH	N-1-OH	N-1-GE	
		2.4	1.8	2.5	3.7	0.4	0.3	2.4	7.0	
		77.4	72.5	49.0	62.3	19.8	25.7	14.2	24.0	
単量体 (B)	含有モル%									
	VdF	-	-	-	-	79.8	66.8	64.1	64.0	
	HFP	-	-	-	-	-	7.2	-	5.0	
	CTFE	-	-	-	-	-	-	19.3	-	
DSC測定 (°C)	E	30.2	25.7	48.5	34.0	-	-	-	-	
	Tg	-	-	-	-	-	-	16	-	
	Tm	235	252	258	223	133	109	-	94	
1%熱分解温度 (°C)	Td	350	384	366	272	374	359	367	283	
GPC分子重 × 10 ⁴ (THF)	Mn	-	-	-	-	7.5	7.1	7.6	6.5	
	Mw	-	-	-	-	21.3	12.1	13.9	11.5	
フロー値 ¹⁾ (ml/sec)		5.3×10 ⁻²	4.1×10 ⁻²	3.9×10 ⁻³	3.2×10 ⁻²	-	-	-	-	
IR分析 (cm ⁻¹)	ν非会合OH	3633	3633	3634	3680~	3628	3624	3633	-	
	ν会合OH	3478	3489	3481	2800	3442	3441	3456	-	
	νC=O	-	-	-	1716	-	-	-	-	

1) 300 °C、7kg荷重下での測定。

Work examples 20-26 Copolymerization with the mixed monomer containing a functional group content fluorine-containing monomer (A) and a fluorine-containing monomer (B) The mixed monomer presentation of the functional group content fluorine-containing monomer (A) of a work example 19, and a monomer (B) (and these

preparation weight), An initiator and a solvent (and the weight), and reaction time were changed into the monomer mixture (and those weight) of a monomer (A) and a monomer (B), initiator, and solvent (and the weight) which were indicated to Table 3, and also the copolymer was obtained by the same method as a work example 19.

However, separation of the copolymer after the end of a reaction was performed [work example / 23 / work examples / 24, 25, and 26] by the same method as a work example 14 the same method as a work example 17 with the same method as a work example 19 about work examples 20, 21, and 22, respectively.

The result of the presentation of the copolymer obtained in the work examples 20-26, a thermal analysis and a flow value, or GPC measurement molecular weight is shown in Table 4.

Work example 27 Copolymerization of perfluoro (1, 1, 9, and 9-tetrahydro 2, 5-screw trifluoromethyl 3, 6-dioxo 8-nonenol), and a tetrafluoroethylene / ethylene mixing monomer Agitator, A valve, a pressure gauge, and a thermometer to the autoclave made from 1l. stainless steel which it had 250ml of pure water, 0.16g of the perfluoro (1, 1, 9, and 9-tetrahydro 2, 5-screw trifluoromethyl 3, 6-dioxo 8-nonenol) obtained in the work example 6 as shown in Table 5 is put in. After nitrogen gas replaced the inside of a system enough, it was made the vacuum, and 1, 2-dichloro 1, 1, and 2, 2-tetrafluoro ethane (R-114) 250g, and Cyclohexane 1.0g were taught, and the inside of a system was kept at 35 degrees C.

Agitating, the monomer mixture of the tetrafluoroethylene/ethylene (molar ratios 82/18) which carried out mixed preparation in the cylinder beforehand was pressed fit so that internal pressure might become 8.0 kgf/cm 2G. Subsequently, 2.0g of 50% methanol solution of di-n-propyl peroxi dicarbonate was pressed fit, and the reaction was started. Since a pressure declines with advance of a polymerization reaction, when it falls to 7.5 kgf/cm 2G Recompression was carried out to 8.0 kgf/cm 2G with the monomer mixture of the tetrafluoroethylene/ethylene (molar ratios 52/48) which carried out mixed preparation in the cylinder separately, pressure lowering and ** pressure were repeated, and tetrafluoroethylene / ethylene (molar ratios 52/48) monomer mixture was supplied. Whenever a mixed monomer consumes about 2.5g from a polymerization start, continuing supply of a mixed monomer furthermore Press fit 0.08g of the aforementioned hydroxy group content fluorine-containing monomer (N-1-OH) a total of 9 times (a total of 0.72g), and a polymerization is continued. From the polymerization start, supply of the mixed monomer was stopped in the time of a mixed monomer consuming about 25g, i.e., the 1.5th hour, the autoclave was cooled, and an unreacted monomer and R-114 were emitted.

It processed by the same method as a work example 18, and 25.6g of white powder was obtained.

表 5

反応条件	実施例番号	27	28	29	30	31	32
官能基含有単量体 (A) 初期仕込み量 (g) 追加仕込み量 (g)		N-1-OH 0.16 0.08 × 9回	N-1-OH 0.16 0.08 × 9回	N-1-OH 0.3 0.15 × 9回	N-1-COOH 0.16 0.08 × 9回	N-1-COOH 0.31 0.16 × 9回	N-1-OH 1.89 0.94 × 9回
	単量体 (B)						
	初期 TFE/E モル比 追加 TFE/E モル比	82/18 52/48	82/18 52/48	82/18 52/48	82/18 52/48	82/18 52/48	82/18 52/48
開始剤		NPP	NPP	NPP	NPP	NPP	NPP
仕込み量 (g)		1.0	1.0	1.0	1.0	1.0	6.0
シクロヘキササン (g)		1.0	1.6	1.6	1.0	1.6	9.6
反応温度 (°C)		35	35	35	35	35	35
反応時間 (hr)		1.5	1.2	1.4	1.5	2.0	1.6

The composition ratio of the obtained copolymer checked existence of a functional group from 19 F-NMR and a ultimate analysis, more nearly respectively than an infrared absorption spectrum.

Moreover, the flow value was measured for the fusing point of the copolymer by DSC using the quantity-ized type flow tester. A result is shown in Table 6.

表 6

実施例番号		27	28	29	30	31	32
重合結果		25.6	22.2	27.5	33.0	50.5	222.8
ポリマー組成	収量 (g)	25.6	22.2	27.5	33.0	50.5	222.8
	官能基含有単量体 (A) 含有モル%	N-1-OH	N-1-OH	N-1-OH	N-1-COOH	N-1-COOH	N-1-OH
	単量体 (B) 含有モル%	0.2	0.2	0.4	0.2	0.5	0.4
融点	T F E	56.3	54.9	54.9	55.0	55.2	56.8
	E	43.5	44.9	44.7	44.8	44.3	42.8
	(°C)	275	277	274	277	274	272
1%熱分解温度 (°C)		359	361	377	368	336	387
フロー値 (ml/sec) 1)		4.3×10^{-3}	2.7×10^{-2}	3.0×10^{-2}	4.0×10^{-3}	2.5×10^{-2}	3.1×10^{-1}
I R 分析 (cm ⁻¹)	ν 非会合 OH	3644	3644	3636	3680	3680	3645
	ν 会合 OH	3356	3350	3355	~2800	~2800	3360
	ν C = O	-	-	-	1789	1789	-

1) 300 °C、7 kg 荷重下での測定。

Work examples 28-31 Copolymerization of a functional group content fluorine-containing monomer (A), and a tetrafluoroethylene / ethylene mixing monomer The functional group content fluorine-containing monomer (A) and its charge of a work example 27, The copolymer was obtained by the same method as a work example 27 except having changed the quantity of the mixed monomer of a monomer (B), an

initiator, and cyclohexane into what was indicated to Table 5.

The result of the copolymerization composition of the copolymer obtained in each work example, a thermal analysis, and a flow value is shown in Table 6.

Work example 32 Copolymerization of perfluoro (1, 1, 9, and 9-tetrahydro 2, 5-screw trifluoromethyl 3, 6-dioxo 8-nonenol), and a tetrafluoroethylene / ethylene mixing monomer Agitator, The autoclave made from 6l. stainless steel equipped with the valve, the pressure gauge, and the thermometer is used. The copolymer was obtained by the same method as a work example 27 the conditions shown in Table 5 except using 1500ml of pure water, 1, 2-dichloro 1, 1, and 2, and 2-tetrafluoro ethane (R-114) 1500g as a solvent. The result of a copolymer presentation, a thermal analysis, and a flow value is shown in Table 6.

Work example 33 Copolymerization of perfluoro (1, 1, 9, and 9-tetrahydro 2, 5-screw trifluoromethyl 3, 6-dioxo 8-nonenol), tetrafluoroethylene, and perfluoro (propyl vinyl ether) An agitator, a valve, a pressure gauge, After it put 1500ml of pure water into the autoclave made from 6l. glass lining equipped with the thermometer and nitrogen gas replaced enough, it was made the vacuum and 1 and 1-dichloro 1, 1, and 2 and 2-tetrafluoro ethane (R-114) 1500g were taught. Subsequently, the perfluoro (1, 1, 9, and 9-tetrahydro 2, 5-screw trifluoromethyl 3, 6-dioxo 8-nonenol) 2.4g obtained in the work example 6 as shown in Table 7, Perfluoro (propyl vinyl ether) (PPVE) 30g and Methanol 210g were pressed fit using nitrogen gas, and the temperature in a system was kept at 35 degrees C.

Agitating, tetrafluoro ethylene was pressed fit so that internal pressure might serve as 8.0 kgf/cm 2G. Subsequently, 2.4g of 50% methanol solution of di-n-propyl peroxi dicarbonate was pressed fit using nitrogen, and the reaction was started.

Since the pressure declined with advance of a polymerization reaction, when it fell to 7.5 kgf/cm 2G, recompression was carried out to 8.0 kgf/cm 2G with tetrafluoro ethylene, and pressure lowering and ** pressure were repeated.

Whenever about 60g of tetrafluoro ethylene is consumed from a polymerization start, continuing supply of tetrafluoroethylene 1.2g of the aforementioned hydroxy group content fluorine-containing monomer (N-1-OH), and 3.3g of perfluoro (propyl vinyl ether) -- respectively -- a total of 9 times (an N-1-OH total -- 10.8g --) a perfluoro (propyl vinyl ether) total -- 29.7g -- it pressed fit and the polymerization was continued, supply was stopped in the time of about 600g of tetrafluoroethylenes being consumed from a polymerization start, i.e., the 5.6th hour, the autoclave was cooled, and an unreacted monomer and R-114 were emitted.

It processed by the same method as a work example 18, and 642g of white powder was obtained. Existence of 19 F-NMR and a functional group was checked for the composition ratio of the obtained copolymer with the infrared absorption spectrum.

Moreover, the flow value was measured for the fusing point of the copolymer by DSC using the quantity-ized type flow tester.

A result is shown in Table 7.

表 7

実施例番号			33	34	35
条件・結果					
官能基含有単量体 (A)			N-1-OH	N-1-OH	N-1-OH
初期仕込み量 (g)			2.4	2.6	5.0
追加仕込み量 (g)			1.2 × 9 回	3.6 × 9 回	3.7 × 9 回
単 量 体 B	TFE 連続仕込み圧力 (kgf/cm ² G)		7.5~8.0	7.5~8.0	7.5~8.0
	PPVE ¹⁾ 初期仕込み量 (g)		30.0	48.6	50.3
	PPVE 追加仕込み量 (g)		3.3 × 9 回	1.3 × 9 回	2.5 × 9 回
開 始 剤			NPP	NPP	NPP
仕込み量 (g)			2.4	2.4	2.4
メタノール量 (g)			210	120	120
反応温度 (℃)			35	35	35
反応時間 (hr)			5.6	5.5	8.0
収 量 (g)			642	671	652
ポリ マー 組成 (モ ル %)	官能基含有単量体 (A)		0.4	0.6	1.0
	単量体 B	TFE	99.2	99.1	98.5
		PPVE	0.4	0.3	0.5
融 点 (℃)			311	309	308
1%熱分解温度 (℃)			369	362	384
フロー値 (ml/sec) ²⁾			2.9 × 10 ⁻³	1.4 × 10 ⁻³	1.7 × 10 ⁻³
IR 分析 (cm ⁻¹)	ν 非会合 OH		3644	3651	3651
	ν 会合 OH		3549	3549	3524

1) PPVE: パーフルオロ (プロピルビニルエーテル)

2) 372 °C、7kg 荷重下での測定。

work examples 34-35 Perfluoro Copolymerization of (9 and 9-dihydro 2, 5-screw trifluoromethyl 3, 6-dioxo 8-nonenol), tetrafluoroethylene, and perfluoro (propyl vinyl ether) The charge of the hydroxyl content fluorine-containing monomer (N-1-OH) of a work example 33, Except having changed the charge, the initiator, and the amount of methanol of perfluoro (propyl vinyl ether) into what was indicated to Table 7, the

polymer was obtained by the same method as a work example 33, and measurement by the same method as a work example 33 was performed.

A result is shown in Table 7.

Work example 36 Emulsification copolymerization of perfluoro (1, 1, 9, and 9-tetrahydro 2, 5-screw trifluoromethyl 3, 6-dioxo 8-nonenol), and a vinylidene fluoride / tetrafluoroethylene / hexafluoropropylene mixing monomer An agitator, a valve, [the 11. glass autoclaves equipped with the pressure gauge and the thermometer] As shown in Table 8, as 500ml of pure water, and an emulsifier Perfluoro octanoic acid ammonium (PFOA) 1.0g, 0.5g of the perfluoro (1, 1, 9, and 9-tetrahydro 2, 5-screw trifluoromethyl 3, 6-dioxo 8-nonenol) obtained in the work example 6 was taught, nitrogen gas replaced the inside of a system enough, and it heated at 60 degrees C.

The vinylidene fluoride / tetrafluoroethylene / hexafluoropropylene which carried out mixed adjustment in the cylinder beforehand while agitating continuously (molar ratio 60/20/20)

The ** monomer mixture was pressed fit so that internal pressure might become 8.0 kgf/cm 2G at 60 degrees C. Subsequently, the solution which dissolved 0.5g of ammonium persulfates (APS) in 5.0ml of pure water was pressed fit using nitrogen gas, and the reaction was started.

表 8

実施例番号		36	37	38	39	40	41	42
反応条件 官能基含有単量体 (A) 初期仕込み量 (g) 追加仕込み量 (g)	N-1-OH	N-1-OH	N-1-OH	N-1-OH	N-1-OH	N-1-OH	N-1-COOH	N-1-COONH ₄
	0.50	2.15	1.13	4.98	4.89	2.20	2.5	
	0.24 × 7回	0.60 × 5回	0.60 × 5回	1.65 × 5回	—	1.15 × 5回	—	
	混合モノマー組成	60	60	60	60	60	74	
単量体 (B)	TFE	20	20	20	20	20	20	14
	HFP	20	20	20	20	20	20	—
	CTFE	—	—	—	—	—	—	12
	乳化剤	PFOA	PFOA	PFOA	PFOA	PFOA	PFOA	—
仕込み量 (g)		1.0	1.0	1.0	1.0	1.0	1.0	—
開始剤	APS	APS	APS	APS	APS	APS	APS	APS
	仕込み量 (g)	0.5	0.5	0.5	0.5	0.5	0.5	0.2
反応温度 (°C)		60	80	60	80	60	80	60
反応時間 (hr)		7.5	5.8	9.1	11.0	4.5	4.8	2.5

Since the pressure declined with advance of a polymerization reaction, when it fell to 7.5 kgf/cm 2G, recompression was carried out to 8.0 kgf/cm 2G with the same VdF/TFE/HFP (molar ratio 60/20/20) monomer mixture as the above, and pressure

lowering and ** pressure were repeated.

Continuing supply of a mixed monomer furthermore, whenever a mixed monomer consumes about 25g from a polymerization start, press fit 0.24g of the aforementioned hydroxy group content fluorine-containing monomer (N-1-OH) a total of 7 times (a total of 1.68g), and a polymerization is continued. From the polymerization start, said autoclave was cooled in the time of consuming about 200g of mixed monomers, i.e., the 7.5th hour, the unreacted monomer was emitted, and the aqueous emulsion was obtained. Coagulation of this aqueous emulsion was frozen and carried out, and the coagulation thing was washed, it dried, and 189g of rubber-like polymers were obtained. Existence of a functional group was checked for the composition ratio of the obtained copolymer from $^1\text{H-NMR}$ and $^{19}\text{F-NMR}$, more nearly respectively than an infrared absorption spectrum.

Moreover, the glass transition point (T_g) of the copolymer was measured by DSC, and molecular weight was measured by GPC analysis of a THF solvent.

A result is shown in Table 9.

表 9

重合結果		実施例番号		36	37	38	39	40	41	42
ポリマ組成	収 量 (g)		189	134	144	141	26.1	147	25.1	
	官能基含有単量体 (A)		N-1-OH	N-1-OH	N-1-OH	N-1-OH	N-1-OH	N-1-COOH	N-1-COONH ₄	
	含有モル%		0.1	0.5	0.4	1.3	2.5	0.4	0.7	
	単量体 (B)	VdF	62.8	63.0	62.4	63.1	66.3	63.5	72.2	
		TfE	18.0	18.5	19.7	18.1	20.4	18.1	13.7	
HFP		19.1	18.0	17.5	17.5	10.8	18.0	-		
CTFE		-	-	-	-	-	-	13.4		
DSC測定 (°C)			Tg	-17.0	-20.8	-17.0	-21.5	-23.0	-17.5	-
			Tm	-	-	-	-	-	-	80.6
1%熱分解温度 (°C)			Td	380	405	369	395	395	353	356
GPC分子重 × 10 ⁴ (THF)			Mn	21.4	7.1	21.6	5.1	6.5	9.2	28.5
			Mw	50.1	12.7	47.4	8.1	14.5	14.2	78.0
I R 分析 (cm ⁻¹) (キャストフィルム)			ν 非会合OH	-	-	-	-	-	3580	3490~2630
			ν 会合OH	3302	3300	3301	3301	3300	~2650	(νNH)
			ν C=O	-	-	-	-	-	1770	1669

Work examples 37-42 Emulsification copolymerization with the monomer mixture which makes a principal component a functional group content fluorine-containing monomer (A) and vinylidene fluoride The kind and initial charge of the functional group content fluorine-containing monomer (A) of a work example 36, an additional charge, and the

number of times, the mixed monomer presentation of a monomer (B), The copolymer was obtained by the same method as a work example 36 except having changed each of an initiator and an emulsifier, reaction temperature, and time at the monomer (A) indicated to Table 8 and its initial charge, an additional charge and the number of times, the monomer mixture of a monomer (B), an initiator, an emulsifier, and polymerization temperature time.

The result of the molecular weight by the presentation of the copolymer obtained in the work examples 37-42, a thermal analysis, and GPC measurement is shown in Table 9. Work example 43 Copolymerization of perfluoro (9 and 9-dihydro 2, 5-screw trifluoromethyl 3, 6-dioxo 8-nonene acid), and a tetrafluoroethylene / perfluoro (methyl vinyl ether) mixing monomer An agitator, a valve, a pressure gauge, [a thermometer] The perfluoro (9 and 9-dihydro 2, 5-screw trifluoromethyl 3, 6-dioxo 8-nonene acid) (N-1-COOH) 2.0g and 1 obtained in 1000ml of pure water, and the work example 5 by the autoclave made from 6l. stainless steel which it had, 1.04g of 4-Joad perfluoro butane (ICF2CF2CF2CF2I) was put in, nitrogen gas replaced the inside of a system enough, and it heated at 80 degrees C.

Agitating continuously, the monomer mixture of the tetrafluoroethylene/perfluoro (methyl vinyl ether) (PMVE) which carried out mixed preparation in the cylinder beforehand (molar ratios 63/37) was pressed fit so that internal pressure might become 8.0 kgf/cm 2G at 80 degrees C. Subsequently, the solution which melted 0.25g of ammonium persulfates (APS) to 5.0ml of pure water was pressed fit using nitrogen gas, and the reaction was started.

since a pressure declines with advance of a polymerization reaction, when you fall to 7.5 kgf/cm 2G, wait 8.0 kgf/cm2G with the same TFE/PMVE (molar ratios 63/37) monomer mixture as the above -- recompression was carried out and pressure lowering and ** pressure were repeated.

From the polymerization start, supply was stopped in the time of a mixed monomer consuming about 200g, i.e., the 21st hour, the autoclave was cooled, the unreacted monomer was emitted, and the aqueous emulsion was obtained.

Coagulation of this aqueous emulsion was carried out by freezing, and the coagulation thing was washed, it dried, and 198g of rubber-like polymers were obtained.

The presentations of the obtained copolymer were TFE/PMVE/N-1-COOH=59.8/39.8 / 0.4 (mole %) from 19 F-NMR and 1 H-NMR analysis. As for the infrared spectrum, characteristics absorption of -OH was observed by 1780cm-1 characteristics absorption of -C=O, and 2640-3580cm-1. -3.4 degree C and the 1% pyrolysis temperature Td of glass-transition temperature (Tg) were 359 degrees C. Mooney viscosity (100 degrees C) was ML1+10=60.

III. the example about a thermoplastics constituent.

The next examination was done in the following examples.

- (1) Tension test By the tensilon universal testing machine made from ORIEN Tech, it is ASTM. According to D638, it measured by crosshead speed 10 mm/min under the room temperature using type5 dumbbell.
- (2) Bending test The tensilon universal testing machine made from ORIEN Tech is used, and it is JIS. According to K-6911, under the room temperature, it bent and measured by velocity 2 mm/min.
- (3) Izod impact test A Kamishima Factory U-F impact testing machine is used, and it is

ASTM. Izod impactive strength with a notch was measured according to D256.

(4) Load deflection temperature Yasuda Energy Machine Factory heat day SUTOSHON tester is used, and it is JIS. According to K7207, it measured under N2 air current on condition of load 18.5kgf/cm², and the heating rate of 2 degrees C / min.

(5) Melt flow rate The melt flow rate (g/10min) was measured in [preheating] 5 minutes using the nozzle 2mm in diameter, and 8mm in length using the Shimadzu Corp. make quantity-ized type flow tester.

(6) Hardness ASTM According to D2240, it measured using the TypeA durometer.

(7) Molding shrinkage ASTM According to D955, the molding shrinkage of the direction of a flow and the direction right-angled with a flow was measured.

(8) Coefficient of linear expansion The coefficient of linear expansion at 40-150 degrees C was measured by load 0.16 kgf/cm² using TMA made from Physical science Electricity.

Example 5 of reference Synthesis of the VdF/TFE/HFP copolymer which does not contain a functional group [with the same method as a work example 36] except not using perfluoro (1, 1, 9, and 9-tetrahydro 2, 5-screw bird KURUORO methyl 3, 6-dioxo 8-nonenol) Vinylidene fluoride / tetrafluoroethylene / hexafluoropropylene copolymer was obtained. [a polymerization reaction / monomer / in a work example 36 / the vinylidene fluoride / tetrafluoroethylene / hexafluoropropylene (presentation molar ratio 60/20/20) mixing monomer] When 150g was consumed (5.5 hours), supply was stopped, the unreacted monomer was emitted, the same treatment as a work example 36 was performed, and 145g of rubber-like polymers were obtained.

The presentations of the obtained polymer were vinylidene fluoride / tetrafluoroethylene / hexafluoropropylene =61.3 / 18.9/19.8mol % from 19 F-NMR and 1 H-NMR. The molecular weight by GPC analysis (THF solvent) was 215000 and the weight average molecular weight 473000 in the number average molecular weight. -17 degree C and 1% pyrolysis temperature were 420 degrees C the glass transition point by DSC measurement.

work example 44 Improvement of the mechanical hardness by the blend of polyphenylene sulfide resin and functional group content fluorine-containing elastomer 44.8g of polyphenylene sulfide resin (TOPUREN T4 made from TOPUREN) is supplied to content volume [three] the Brabender mixer of 60cm set as 300 degrees C. After carrying out melting for 4 minutes at the number of rotations of 50rpm, 15.1g of hydroxyl content fluorine-containing elastomer obtained in the work example 38 was added, and it kneaded for 6 minutes at the number of rotations of 100rpm. In this case, compared with the comparative example 1 which carries out a postscript, the degree of the torque rise at the time of mixing was large. Compression molding of the obtained constituent was carried out at 300 degrees C, and the specimen was produced. The bending test and the Izod impact test were done using the obtained specimen. A result is shown in Table 10.

表 10

試験結果		実施例	比較例	
		44	1	2
組成 (重量%)	官能基含有含フッ素ポリマー (D)			
	実施例 38	20	—	—
	熱可塑性樹脂 (E)			
	ポリアリーレンサルファイド	80	80	100
成形物の性質	その他ポリマー (F)			
	参考例 5	—	20	—
	曲げ強度 (kgf/cm^2)	780	570	1150
	曲げ弾性率 (kgf/cm^2)	38700	35000	37000
	アイゾット衝撃強度 ($\text{kgf} \cdot \text{cm}/\text{cm}$)	3.4	1.4	1.3

Comparative example 1 Except having used the fluorine-containing elastomer which does not contain the functional group which changed to the hydroxyl content fluorine-containing elastomer obtained in the work example 38, and was obtained in the example 5 of reference, kneading shaping was carried out by the same method as a work example 44, and the specimen was produced. A result is shown in Table 10.

Comparative example 2 Compression molding of the polyphenyl sulfide resin (the same thing as a work example 44) was carried out at 300 degrees C, and the specimen was produced. The same examination as a work example 44 was done. A result is shown in Table 10.

By blending the fluorine-containing elastomer which introduced hydroxyl so that clearly from the result of Table 10 to polyphenylene sulfide resin (work example 44) Izod impactive strength can be more effectively improved without reducing a mechanical property remarkably compared with the blend (comparative example 1) of the fluorine-containing elastomer which does not contain a functional group.

work example 45 blend of polyamide resin and functional group content fluorine-containing elastomer Polyamide 12 (made by Ube Industries, Ltd. UBE Nylon 12) 3024B) [22.5 g] After supplying to the content volume [three] Brabender mixer of 60cm set as 190 degrees C and carrying out melting for 2 minutes at the number of rotations of 10rpm, 33.8g of carboxyl group content fluorine-containing elastomer obtained in the work example 41 with the number of rotations of 50rpm was added, and it kneaded for 5 minutes at the number of rotations of 100rpm. Compression molding of the obtained constituent was carried out at 200 degrees C, and the specimen was produced. A result is shown in Table 11.

表 11

実施例番号 試験結果		45	46	47	48	49	50	51
組成 (重量%)	官能基含有含フッ素ポリマー (D)							
	実施例 18 の重合体	—	—	5	10	—	—	—
	実施例 22 の重合体	—	—	—	—	—	5	10
	実施例 26 の重合体	—	—	—	—	5	—	—
	実施例 41 の重合体	60	30	—	—	—	—	—
	熱可塑性樹脂 (E)							
	ポリアミド 12	40	70	70	70	70	70	70
	官能基非含有含フッ素ポリマー (F)							
成形物の性質	P V d F 1)	—	—	25	20	25	—	—
	E T F E 2)	—	—	—	—	—	25	20
	(引張試験)							
	引張強度 (kgf/cm ²)	166	376	460	430	458	390	360
	引張弾性率 (kgf/cm ²)	3900	7600	10700	12900	9900	10400	11900
	(耐薬品性試験)							
	体積変化率 (%)	—	15.7	10.4	11.3	12.8	10.9	10.4
	強度保持率 ³⁾ (%)	—	102	102	97	88	85	80

1) ダイキン工業 (株) 製 ネフロン VDF VP-800

2) ダイキン工業 (株) 製 ネフロン ETFE EP-610

3) [(耐薬品性試験後の引張強度) / (試験前の引張強度)] × 100

The vinylidene fluoride / tetrafluoroethylene / hexafluoropropylene copolymer which does not contain a functional group instead of the carboxyl group content fluorine-containing polymer obtained in the comparative example 3 work example 41 (Daikin Industries, LTD.)

** Except having used DAIERU G902, kneading and shaping were performed by the same method as a work example 45, and the specimen was produced. A result is shown in Table 12.

表 12

比較例番号 試験結果		3	4	5	6	7	8
組成 (重量%)	熱可塑性樹脂 (D)						
	ポリアミド 12	40	70	70	70	70	100
	官能基非含有含フッ素ポリマー (F)						
	VdF/TFE/HFP 共重合体(含フッ素 エラストマー) 1)	60	30	—	—	—	—
	P V d F 2)	—	—	30	—	25	—
成形物の 性質	E T F E 3)	—	—	—	30	—	—
	その他 4)						
	アクリル系相溶剤	—	—	—	—	5	—
	(引張試験)						
	引張強度 (kgf/cm ²)	32	287	453	350	471	416
性質	引張弾性率 (kgf/cm ²)	640	6600	9600	9400	9300	8000
	(耐薬品性試験)						
	体積変化率 (%)	—	15.8	11.5	14	28	15.8
	強度保持率 5) (%)	—	70	57.2	48.3	53	74

1) ダイキン工業 (株) 製 ダイエル G902

2) ダイキン工業 (株) 製 ネフロン VDF VP-800

3) ダイキン工業 (株) 製 ネフロン ETFE EP-610

4) 東亜合成化学工業 (株) 製 レゼダ GP300

5) [(耐薬品性試験後の引張強度) / (試験前の引張強度)] × 100

The result of the tension test of a work example 45 (Table 11) and a comparative example 3 (Table 12) is compared, and in the blend with polyamide, improvement with large tensile strength and value of a modulus of elasticity in tension is obtained by introducing a carboxyl group into fluorine-containing polymer so that clearly.

Work example 46 [with the blend of polyamide resin and functional group content fluorine-containing elastomer] Improvement of medicine-proof Except using 14.2g of carboxyl group content fluorine-containing elastomer obtained in polyamide 12 (it is the

same as work example 45) 33.2g, and the work example 41, kneading and shaping were performed by the same method as a work example 45, and the specimen was produced. The tension test and chemical corrosion resistance test of the specimen which were obtained were done.

(Chemical corrosion resistance test)

According to JIS-K630, a volume change and strength retention after being immersed at 50 degrees C for 72 hours were measured using toluene / isooctane / methanol =40/40 / 20 (volume %) partially aromatic solvent.

A result is shown in Table 11.

Comparative example 4 Except having used the fluorine-containing elastomer (it being the same as a comparative example 3) which changes into the carboxyl group content fluorine-containing elastomer obtained in the work example 41, and does not contain a functional group, kneading shaping was performed by the same method as a work example 46, and the specimen was produced. A result is shown in Table 12.

Work example 47 Addition of the functional group content fluorine-containing polymer to polyamide resin and the blend thing of PVdF Supply polyamide 12 (it is the same as work example 45) 32.7g to the content volume [three] blender mixer of 60cm set at 210 degrees C, and it fuses for 2 minutes at the number of rotations of 10rpm. After adding PVDF(Daikin Industries, LTD. make neo chlorofluocarbon VDF VP-800)11.7g and mixing for 2 minutes, at 50rpm, the carboxyl group content fluorine-containing polymer 2.3g of the work example 18 was added, and number of rotations was kneaded for number-of-rotations 100rpm 5 minutes.

Compression molding of the obtained constituent was carried out at 210 degrees C, and the specimen was produced. A result is shown in Table 11.

Work example 48 Addition of the functional group content fluorine-containing polymer to polyamide resin and the blend thing of PVdF PVdF(it is the same as work example 47) 9.3g, Except having used the carboxyl group content fluorine-containing polymer 4.7g of the work example 18, it fabricated by having kneaded like the work example 47, and the specimen was produced. A result is shown in Table 11.

Work example 49 Addition of the functional group content fluorine-containing polymer to polyamide resin and the blend thing of PVdF [the glycidyl group content fluorine-containing polymer which changed to the carboxyl group content fluorine-containing polymer obtained in the work example 18, and was obtained in the work example 26] Except having used, kneading shaping was performed like the work example 47, and the specimen was obtained.

Work example 50 Addition of the functional group content fluorine-containing polymer to polyamide resin and the blend thing of ETFE Polyamide 12 (it is the same as work example 45) 33.0g is supplied to the content volume [three] blender mixer of 60cm set at 240 degrees C. After fusing for 2 minutes at the number of rotations of 10rpm, adding ETFE(Daikin Industries, LTD. make neo chlorofluocarbon ETFE EP-610)11.8g and mixing for 2 minutes, The carboxyl group content fluorine-containing polymer 2.4g obtained in the work example 22 with the number of rotations of 50rpm was added, and it kneaded for 5 minutes at the number of rotations of 100rpm.

Compression molding of the obtained constituent was carried out at 240 degrees C, and the specimen was produced.

A result is shown in Table 11.

Work example 51 Addition of the functional group content fluorine-containing polymer to polyamide resin and the blend thing of ETFE It is made to be the same as that of a work example 50 except having used the carboxyl group content fluorine-containing polymer 4.8g obtained in ETFE(it is the same as work example 50)9.4g, and the work example 22. Kneading shaping was performed and the specimen was produced. A result is shown in Table 11.

Comparative example 5 After supplying polyamide 12 (it is the same as work example 45) 32.7g to the blender mixer set as 210 degrees C and fusing for 2 minutes at the number of rotations of 10rpm, PVDf(it is the same as work example 47)14.0g was added, and it kneaded for 5 minutes at the number of rotations of 100rpm. The specimen was produced by the same method as a work example 47. A result is shown in Table 12.

Comparative example 6 After supplying polyamide 12 (it is the same as work example 45) 33.0g to the blender mixer set as 240 degrees C and fusing for 2 minutes at the number of rotations of 10rpm, ETFE(it is the same as work example 50)14.2g was added, and it kneaded for 5 minutes at the number of rotations of 100rpm. The specimen was produced by the same method as a work example 50. A result is shown in Table 12.

Comparative example 7 It changes to the carboxy group content fluorine-containing polymer obtained in the work example 18. Except having used the compatibilizer (product REZEDAGPmade from Toagosei Chemical industry300) of the epoxy conversion polystyrene acrylic graft polymer system, kneading and shaping were performed like the work example 47, and the specimen was produced. A result is shown in Table 12.

Comparative example 8 Compression molding of the polyamide 12 (it is the same as a work example 45) was carried out at 190 degrees C, and the specimen was produced. A result is shown in Table 12.

A good mechanical property and chemical resistance are obtained by blending carboxyl group content fluorine-containing polymer or glycidyl group content fluorine-containing polymer to polyamide resin so that clearly from each test result of the work examples 46-51 of Table 11.

[the blend thing (comparative examples 4-6 of Table 12) of the fluorine-containing polymer and polyamide which do not contain a functional group in particular] The tensile strength fall after a chemical corrosion resistance test was remarkable, and although the improvement in early tensile strength was found, as for what added the compatibilizer of the epoxy conversion polystyrene acrylic graft polymer system (comparative example 7), hardness fell remarkably after the chemical corrosion resistance test.

On the other hand, what blended carboxyl group content fluorine-containing polymer, glycidyl group content fluorine-containing polymer, and polyamide showed tensile strength even with after [good] a chemical corrosion resistance test while showing the good mechanical property. That is, by introducing a functional group into fluorine-containing polymer showed that the constituent which has improved the dispersibility of the fluorine-containing polymer in a blend thing with polyamide and an interface adhesive property could be obtained.

Work example 52 Blend of liquid crystal polyester and hydroxyl content fluorine-containing elastomer 26.0g of liquid crystal polyester (nova curate E310 by Mitsubishi Kasei Corp.) is fed into content volume [three] the Brabender mixer of 60m set as 200

degrees C. After carrying out melting for 1 minute and 30 seconds at the number of rotations of 10rpm, 38.9g of hydroxy group content fluorine-containing elastomer obtained in the work example 36 with the number of rotations of 50rpm was added, and it kneaded for 5 minutes at the number of rotations of 100rpm. Compression molding of the obtained constituent was carried out at 200 degrees C, and the specimen was produced. The tension test was done using the specimen. A result is shown in Table 13.

表 13

試験結果	実施例					比較例		
	52	53	54	55	56	9	10	11
官能基含有フッ素ポリマー(D)								
実施例 36 の重合体	60	-	30	-	30	-	-	-
実施例 37 の重合体	-	60	-	30	-	-	-	-
熱可塑性樹脂 (E)								
液晶ポリエステル (I) 1)	40	40	70	70	-	40	70	-
液晶ポリエステル (II) 2)	-	-	-	-	70	-	-	70
官能基非含有フッ素重合体(F)								
VdF/TFE/HFP 共重合体3) (エラストマー)	-	-	-	-	-	60	30	30
組成物の性質								
(引張試験)								
引張強度 (kgf/cm ²)	115	151	360	333	692	22.9	215	560
引張弾性率 (kgf/cm ²)	4100	3400	15000	12700	23100	480	9800	17900
切断表面の電子顕微鏡写真	-	-	-	図 2	図 3	-	図 4	図 5

1) 三聚化成 (株) 製 ノバキュレート E310

2) ポリブラスチックス (株) 製 ベクトラ A950

3) ダイキン工業 (株) 製 ダイエル® G902

Work example 53 Blend of liquid crystal polyester and hydroxyl content fluorine-containing elastomer Except having used the hydroxyl content fluorine-containing elastomer obtained in the work example 37, kneading shaping was performed by the same method as a work example 52, and the specimen was produced. A result is shown in

Table 13.

work examples 54-55 Blend of liquid crystal polyester and hydroxyl content fluorine-containing elastomer [the hydroxyl content fluorine-containing elastomer obtained in 41.1g of liquid crystal polyester (it is the same as a work example 52), the work example 36 (work example 54), or the work example 37 (work example 55)] Except using 17.6g, respectively, kneading and shaping were performed by the same method as a work example 52, and the specimen was produced about each presentation. A result is shown in Table 13.

Work example 56 Blend of liquid crystal polyester and hydroxyl content fluorine-containing elastomer 42.5g of liquid crystal polyester (Polyplastics Vectra A950) is used. Kneading and shaping were performed by the same method as a work example 54 at 300 degrees C using 18.2g of hydroxyl content fluorine-containing elastomer obtained in the work example 36 except kneading and carrying out compression molding, and the specimen was produced. A result is shown in Table 13.

Comparative examples 9-11 A comparative example 9 using the fluorine-containing elastomer (it is the same as a comparative example 3) which changes to hydroxyl content fluorine-containing elastomer, and does not contain a functional group Work example 52, The work example 54 and the comparative example 11 performed kneading and shaping by the same method as a work example 56, respectively, and the comparative example 10 produced the specimen. A result is shown in Table 13.

Moreover, the freezing fracture of each mold goods obtained by the work example 55, the work example 56, the comparative example 10, and the comparative example 11 was carried out in liquid nitrogen, and the section was observed with the scanning type electron microscope. The enlargement on the surface of cutting (x500) is shown in [drawing 2](#), [drawing 3](#), [drawing 4](#), and [drawing 5](#), respectively.

That is, by blending the fluorine-containing elastomer which introduced hydroxyl so that more clearly than the result of Table 13 to liquid crystal polyester (work examples 52-56) Compared with the case (comparative examples 9-11) where conventional fluorine-containing elastomer is blended, a mechanical property (tensile strength and modulus of elasticity in tension) can be raised sharply.

Moreover, the Plastic solid ([drawing 2](#), [drawing 3](#)) using a hydroxyl content elastomer can check signs that liquid crystal polyester is made into a matrix and fluorine-containing elastomer is carrying out fine dispersion so that clearly, even if it compares the enlargement of each fracture surface of [drawing 2](#), [drawing 4](#) and [drawing 3](#), and [drawing 5](#) .

It is surmised by introducing hydroxyl into fluorine-containing polymer that a reaction produces that it is also partial with liquid crystal polyester, mutual dispersibility is raised, and mechanical hardness is raised more effectively as a result.

Work example 57 Addition of the functional group content fluorine-containing polymer to the blend thing of liquid crystal polyester and PVdF 21.7g of liquid crystal polyester (it is the same as a work example 52) is fed into the content volume [three] blender mixer of 60cm set at 200 degrees C. After having fused for 1 minute and 30 seconds at the number of rotations of 10rpm, adding PVdF(it is the same as work example 47)38.3g and mixing for 2 minutes, the hydroxyl content fluorine-containing polymer 3.8g obtained in the work example 17 at 50rpm in number of rotations was added, and the number of

rotations of 100rpm kneaded for 5 minutes. The obtained constituent was ground, it fabricated with the injection molding machine with cylinder temperature the tool temperature of 80 degrees C of 200-250 degrees C, and the specimen was produced. The tension test of the obtained specimen, a bending test, and measurement of the melt flow rate were performed. A result is shown in Table 14.

表 14

試験結果		実施例		比較例	
		57	58	12	13
組成 (重量%)	官能基含有含フッ素ポリマー(D)				
	実施例17の重合体	5	—	—	—
	実施例37の重合体	—	5	—	—
	熱可塑性樹脂(E)				
	液晶ポリエステル(I) 1)	35	35	35	35
	官能基非含有含フッ素ポリマー(F)				
組成物の性質	PVdF 2)	60	60	60	65
	VdF/TFE/HFP共重合体3) (エラストマー)	—	—	5	—
	(引張試験)				
	引張強度 (kgf/cm ²)	735	675	642	720
	引張弾性率 (kgf/cm ²)	30400	30200	29000	28400
	(曲げ試験)				
	曲げ強度 (kgf/cm ²)	770	741	476	573
	曲げ弾性率 (kgf/cm ²)	27500	27500	24300	27300
	メルトフローレート 4) (g/10min)	46.2	52.5	65.6	65.8

1) 三菱化成(株)製 ノバキュレートE310

2) ダイキン工業(株)製 ネオフロンVDF VP-800

3) ダイキン工業(株)製 ダイエルG902

4) 荷重5kgf/cm²、250℃

work example 58 Liquid crystal polyester PVdF addition of the functional group content fluorine-containing polymer to a ** blend thing the hydroxyl content fluorine-containing polymer 4.4g of 24.5g of liquid crystal polyester (the same as a work example 52), PVdF(the same as work example 47)43.2g, and a work example 37 -- [with the same method as a work example 57] except using Kneading and shaping were performed and the specimen was produced. A result is shown in Table 14.

Comparative example 12 It changed to the hydroxyl content fluorine-containing polymer obtained in the work example 17, and except having used the VdF/TFE/HFP copolymer (it being the same as a comparative example 3) which does not contain a functional group, it kneaded and fabricated by the same method as a work example 57, and the specimen was produced. A result is shown in Table 14.

Comparative example 13 After feeding 24.4g of liquid crystal polyester (it is the same as a work example 52) into the blender mixer set as 200 degrees C and making it dissolve for 1 minute and 30 seconds at the number of rotations of 10rpm, PVdF(it is the same as work example 47)47.4g was added at the number of rotations of 50rpm, and it kneaded at 100rpm. The obtained constituent was fabricated by the same method as a work example 57, and the specimen was produced. A result is shown in Table 14.

adding hydroxyl content fluorine-containing polymer at the time of liquid crystal polyester and the blend of PVdF so that more clearly than Table 14 -- a modulus of elasticity in tension -- it bends and improvement in characteristics and moldability is found.

Although liquid crystal polyester can carry out an orientation and tensile strength etc. can be improved to profit of PVdF to the molding direction at the time of injection molding at the time of liquid crystal polyester and the mere blend of PVdF since dispersibility and the interface adhesive property are inadequate -- especially -- the characteristics of an orientation and a perpendicular direction -- that is, it bends and becomes inadequate [characteristics]. improving dispersibility and an interface adhesive property by adding functional group content fluorine-containing polymer to it in the case of the blend with liquid crystal polyester and PVdF -- a modulus of elasticity in tension -- it can bend and characteristics can be raised more.

Work examples 59-60 It is addition of functional group content fluorine-containing polymer at the time of the blend with PVdF and liquid crystal polyester (II). [the hydroxyl content fluorine-containing polymer obtained in PVdF (it is the same as a work example 47), liquid crystal polyester (it is the same as a work example 56), and the work example 38] After blending uniformly by the presentation shown in Table 15, the biaxial extruder performed kneading and extrusion at 280-300 degrees C, and the pellet was created. The specimen was created with the injection molding machine using this pellet with the cylinder temperature of 240-290 degrees C, and the tool temperature of 50 degrees C, and measurement of a tension test, a bending test, and load deflection temperature was performed. A result is shown in Table 15.

表 15

試験結果		実施例		比較例		
		59	60	14	15	16
組成 (重量%)	官能基含有含フッ素ポリマー(D)					
	実施例 38 の重合体	3	6	—	—	—
	熱可塑性樹脂 (E)					
	液晶ポリエステル (II) 1)	20	20	20	20	—
	官能基非含有含フッ素ポリマー(F)					
組成物の性質	PVdF 2)	77	74	77	80	100
	VdF / TFE / HFP 共重合体 3) (エラストマー)	—	—	3	—	—
	(引張試験)					
	引張強度 (kgf/cm ²)	745	766	710	790	720
	引張弾性率 (kgf/cm ²)	27200	27900	25900	26400	11400
	(曲げ試験)					
	曲げ強度 (kgf/cm ²)	770	740	760	780	680
	曲げ弾性率 (kgf/cm ²)	39300	38300	37700	38500	13700
	荷重たわみ温度 (°C)	150.0	150.4	140.7	130.8	108.0
	メルトフローレート 4) (g/10min)	117	125	108	104	45.2 5) (35.1)

1) ポリプラスチックス (株) 製 ベクトラ A950

2) ダイキン工業 (株) 製 ネフロン VDF VP-800

3) ダイキン工業 (株) 製 ダイエル G902

4) 荷重 5kgf/cm²、300 °C

5) () 内は荷重 5kgf/cm²、250 °C での測定値

Comparative example 14 What blended uniformly the VdF/TFE/HFP copolymer (it is the same as a comparative example 3) which does not contain PVdF (it is the same as a work example 47), liquid crystal polyester (it is the same as a work example 56), and a functional group to the presentation of Table 15 is used. It kneaded with the extruder by the same method as a work example 59, and the specimen was produced with injection molding. A result is shown in Table 15.

Comparative example 15 It kneaded and fabricated like the work example 59 using PVdF (it is the same as a work example 47), and liquid crystal polyester (work example 56),

and the specimen was produced. A result is shown in Table 15.

Comparative example 16 Injection molding was carried out by the same method as a work example 59 using the PVdF (it is the same as work example 47) pellet, and the specimen was obtained. A result is shown in Table 15.

By adding hydroxyl content fluorine-containing polymer from the result of Table 15 at the time of kneading extrusion of PVdF and liquid crystal polyester, [the injection-molded product] Compared with what only blended PVdF and liquid crystal polyester, the load deflection temperature of PVdF and moldability can be improved more effectively.

A work example 61 and comparative examples 17-18 It is addition of functional group content fluorine-containing polymer at the time of the blend with ETFE and liquid crystal polyester (III). ETFE (Daikin Industries, LTD. make neo chlorofluorocarbon ETFE EP-521), After blending uniformly the hydroxyl content fluorine-containing polymer obtained in liquid crystal polyester (SUMIKASU Per LCPby Sumitomo Chemical Co., Ltd. E7000), and the work example 32 using a locking mixer by the presentation shown in Table 16, Kneading and extrusion were carried out at 280-300 degrees C with the biaxial extruder, and the pellet was created. The specimen was created with the injection molding machine using this pellet with the cylinder temperature of 280-320 degrees C, and the tool temperature of 100 degrees C, and measurement of molding shrinkage, a tension test, a bending test, a coefficient of linear expansion, and load deflection temperature was performed. A result is shown in Table 16.

表 16

試験結果		実施例		
		61	17	18
組成 (重量%)	官能基含有含フッ素ポリマー(D)			
	実施例32の重合体	5	—	—
	熱可塑性樹脂(E)			
	液晶ポリエステル(III) 1)	20	20	—
組成物の性質	官能基非含有含フッ素ポリマー(F)			
	ETFE 2)	75	80	100
	(成形収縮率)			
	流動方向(%)	0.07	0.15	1.95
	垂直方向(%)	3.60	3.74	3.91
	(引張試験)			
	引張強度(kgf/cm ²)	360	320	360
	引張弾性率(kgf/cm ²)	20500	18000	6300
	(曲げ試験)			
	曲げ強度(kgf/cm ²)	485	472	—
	曲げ弾性率(kgf/cm ²)	31400	29600	—
	線膨張係数($\times 10^5/^\circ\text{C}$) 3)	3.2	3.70	7.14
	荷重たわみ温度(°C)	118	105	82.2

1) 住友化学(株)製スミカスパーLCP E7000

2) ダイキン工業(株)製ネオフロンETFE EP-521

3) 40~150°C

Work examples 62-64 and comparative examples 19-20 It is addition of functional group content fluorine-containing polymer at the time of the blend with PFA and liquid crystal polyester (IV). PFA (Daikin Industries, LTD. make neo chlorofluorocarbon PFA AP-201), [the hydroxyl content fluorine-containing polymer obtained in liquid crystal polyester (SUMIKASU Per LCPby Sumitomo Chemical Co., Ltd. E6000) and the work example 34, or the work example 35 / the presentation shown in Table 17] After blending uniformly using a locking mixer, the biaxial extruder performed kneading and extrusion at 350-370 degrees C, and the pellet was created. The specimen was created with the injection molding machine using this pellet with the cylinder temperature of 340-360

degrees C, and the tool temperature of 190 degrees C, and the same measurement as a work example 61 was performed. A result is shown in Table 17.

表 17

		実施例			比較例	
		62	63	64	19	20
組成 (重量%)	官能基含有含フッ素ポリマー(D)					
	実施例 34 の重合体	—	—	10	—	—
	実施例 35 の重合体	2	5	—	—	—
	熱可塑性樹脂 (E)					
	液晶ポリエステル (IV) ¹⁾	30	30	30	30	—
組成物の性質	官能基非含有含フッ素ポリマー(F)					
	PFA ²⁾	68	65	60	70	100
	(成形収縮率)					
	流動方向 (%)	-0.37	-0.38	-0.38	-0.34	4.3
	垂直方向 (%)	4.2	4.0	3.4	4.3	4.0
	(引張試験)					
	引張強度 (kgf/cm ²)	535	506	485	470	181
	引張弾性率 (kgf/cm ²)	29200	30600	28600	25200	4100
	(曲げ試験)					
	曲げ強度 (kgf/cm ²)	503	480	478	465	193
	曲げ弾性率 (kgf/cm ²)	49800	47600	47600	43000	5600
	線膨張係数 ($\times 10^5 / ^\circ\text{C}$) ³⁾	2.36	2.26	2.21	2.63	8.91
	荷重たわみ温度 ($^\circ\text{C}$)	247	249	251	235	64

1) 住友化学 (株) 製スミカスーパール LCP E6000

2) ダイキン工業 (株) 製ネオフロン PFA AP-201

3) 40~150℃

At the time of the blend with ETFE, PFA, and liquid crystal polyester, by adding hydroxy group content fluorine-containing polymer, it can do [improving the mechanical property of a Plastic solid, and dimensional stability or], and especially a coefficient of linear expansion and load deflection temperature can be more effectively improved from the result of Table 16 and Table 17.

Work example 65 Thermoplastic elastomer composition by the melting blend with

hydroxyl content fluorine-containing elastomer and liquid crystal polyester 8.2g of liquid crystal polyester (it is the same as a work example 52), Except having used 73.5g of hydroxyl content fluorine-containing elastomer obtained in the work example 36, it kneaded and fabricated like the work example 52, the specimen was produced, and a tension test, melt float, and measurement of hardness (Shore A) were performed. A result is shown in Table 18.

表 18

試験結果		実施例				比較例		
		65	66	67	68	21	22	23
組成	官能基含有含フッ素ポリマー (D)							
	実施例 36 の重合体	90	-	-	-	-	-	-
	実施例 38 の重合体	-	90	85	80	-	-	-
(重量%)	熱可塑性樹脂 (E)							
	液晶ポリエステル (I) 1)	10	10	15	20	10	15	20
	官能基非含有含フッ素ポリマー (F) VdF/TFE/HFP 共重合体 2) (エラストマー)	-	-	-	-	90	85	80
組成物の性質	(引張試験) 3)							
	引張強度 (kgf/cm ²)	41.6	51.4	56.4	62.4	(6.3) 4)	(5.7)	(7.5)
	伸び (%)	405	530	390	210	不定 5)	不定	不定
	メルトフローレート 6) (g/10min)	3.56	9.90	20.2	39.1	-	-	-
硬度 (HsA)		56	55	72	83	40	44	62

1) 三菱化成 (株) 製 ノバキレート E310

2) ダイキン工業 (株) 製 タイエル G902

3) クロスヘッドスピード 10mm/min

4) 最大点強度

5) 低応力伸長で破断せず

6) 荷重 20kgf/cm²、250℃

Work example 66 Thermoplastic elastomer composition by the melting blend with hydroxyl content fluorine-containing elastomer and liquid crystal polyester except having used the hydroxyl content fluorine-containing elastomer obtained in the work example 38. It kneaded and fabricated by the same method as a work example 65, and the specimen was produced. A result is shown in Table 18.

Work example 67 Thermoplastic elastomer composition by the melting blend with hydroxyl content fluorine-containing elastomer and liquid crystal polyester 10.7g of liquid crystal polyester (it is the same as a work example 52), Except using 60.6g of hydroxyl content fluorine-containing elastomer obtained in the work example 38, kneading shaping was carried out like the work example 65, and the specimen was produced. A result is shown in Table 18.

Work example 68 Thermoplastic elastomer composition by the melting blend with hydroxyl content fluorine-containing elastomer and liquid crystal polyester 13.9g of liquid crystal polyester (it is the same as a work example 52), Except using 55.9g of hydroxyl content fluorine-containing elastomer obtained in the work example 38, kneading shaping was carried out like the work example 65, and the specimen was produced. A result is shown in Table 18.

Comparative examples 21-23 A comparative example 21 using the fluorine-containing elastomer (it is the same as a comparative example 3) which changes to hydroxyl content fluorine-containing elastomer, and does not have a functional group. Work example 65, The work example 67 and the comparative example 23 performed kneading and shaping by the respectively same method as a work example 68, and the comparative example 22 produced the specimen. A result is shown in Table 18.

Moreover, the stress-strain curve in the tension test of the mold goods obtained by work examples 66, 67, and 68 and a comparative example 22 is shown in [drawing 6](#).

To extension, what carried out the melting blend of the fluorine-containing elastomer which introduced hydroxyl, and the liquid crystal polyester in the specific presentation range (work examples 65, 66, 67, and 68) shows a high stress, and has bridge formation rubber physical properties so that clearly from Table 18 and [drawing 6](#). Since what blended the fluorine-containing elastomer which furthermore introduced hydroxyl, and liquid crystal polyester shows high temperature flowability, it has the character as a thermoplastic elastomer.

Moreover, in the specific presentation range, it can deal in the thermoplastic elastomer of various hardness by choosing the composition ratio of hydroxyl content fluorine-containing elastomer in a constituent, and liquid crystal polyester.

On the other hand, since it is the mere blend thing of unvulcanized rubber and liquid crystal polyester which blended the fluorine-containing elastomer which does not contain a functional group (comparative examples 21, 22, and 23), even if it shows hot flowability, it shows only low stress to extension, and does not have rubber elasticity.

Work example 69 It is addition of functional group content fluorine-containing polymer at the time of the blend of polycarbonate and ETFE. Polycarbonate (Teijin Chemicals bread-making Rheyd L-1225WP) 31.3g is supplied to the Brabender mixer set as 290 degrees C. After having fused for 2 minutes at the number of rotations of 10rpm, adding ETFE(it is the same as work example 50)7.2g and mixing for 2 minutes, the hydroxyl content fluorine-containing polymer 1.5g of the work example 19 was added at the number of rotations of 50rpm, and it kneaded for 5 minutes at the number of rotations of

100rpm.

Compression molding of the obtained constituent was carried out at 290 degrees C, the specimen was produced, and the tension test and the solvent resistance examination were done.

The solvent resistance examination was done by the following method.

(Solvent resistance examination)

The specimen was made immersed into toluene, it put into the thermostat, and 25 degrees C was neglected for 48 hours. The volume change of the moldings after an examination was measured.

A result is shown in Table 19.

表 19

試験結果		実施例	比較例	
		69	24	25
組成 (重量%)	官能基含有含フッ素ポリマー(D)			
	実施例 19 の重合体	5	—	—
	熱可塑性樹脂 (E)			
	ポリカーボネート	70	70	100
組成物の性質	官能基非含有含フッ素ポリマー ETFE 1)	25	30	0
	(引張試験)			
	引張強度 (kgf/cm^2)	425	419	670
	引張弾性率 (kgf/cm^2)	13300	10700	13100
	(耐溶剤性試験) 2)			
	体積変化率 (%)	25	47	58

1) ダイキン工業(株)製 ネフロンETFE、EP-610

2) トルエン中 25℃、48時間浸漬試験

Comparative example 24 After supplying Polycarbonate (it is the same as a work example 69) 37.6g to the Brabender mixer set as 290 degrees C and carrying out melting for 2 minutes at the number of rotations of 10rpm, ETFE(it is the same as work example 50)16.1g was added at the number of rotations of 50rpm, and it kneaded at the number of rotations of 100rpm. The specimen was produced like the work example 69. A result is shown in Table 19.

Comparative example 25 It fabricated by the same method as a work example 69 using polycarbonate (it is the same as a work example 69), and the specimen was produced. A result is shown in Table 19.

By adding hydroxyl content fluorine-containing polymer at the time of the blend of polycarbonate and ETFE so that more clearly than the result of Table 19 The solvent

resistance of polycarbonate can be improved effectively, without reducing a mechanical property compared with the mere blend thing of polycarbonate and ETFE.

Work example 70 39.0g of liquid crystal polyester (it is the same as a work example 62) is fed into content volume [three] the Brabender mixer of 60cm set as 370 degrees C.

Melting was carried out for 3 minutes at the number of rotations of 10rpm, the hydroxyl content fluorine-containing polymer 39.0g obtained in the work example 35 with the number of rotations of 50rpm was added, and it kneaded for 5 minutes at the number of rotations of 100rpm further.

The obtained constituent was ground, the cylinder temperature of 320-360 degrees C was produced with the injection molding machine, the specimen was produced with the tool temperature of 190 degrees C, and molding shrinkage, the tension test, and the bending test were done. A result is shown in Table 20.

Comparative example 26 Except having changed to hydroxyl content fluorine-containing polymer, and having used PFA (it being the same as a work example 62), it fabricated by having kneaded like the work example 70, and the specimen was produced. A result is shown in Table 20.

表 20

試験結果		実施例 70	比較例 26
組成 (重量%)	官能基含有含フッ素ポリマー(D)		
	実施例 35 の重合体	50	—
	熱可塑性樹脂 (E)		
	液晶ポリエステル (IV) 1)	50	50
組成物の性質	官能基非含有含フッ素ポリマー(F)		
	PFA 2)	—	50
	(成形収縮率)		
	流動方向 (%)	0.14	0.11
組成物の性質	垂直方向 (%)	2.71	2.43
	(引張試験)		
	引張強度 (kgf/cm ²)	1080	660
	引張弾性率 (kgf/cm ²)	52100	43700
組成物の性質	(曲げ試験)		
	曲げ強度 (kgf/cm ²)	625	365
	曲げ弾性率 (kgf/cm ²)	42000	46600

1) 住友化学 (株) 製スミカスーパール CP E6000

2) ダイキン工業 (株) 製ネオフロン PFA AP-201

Industrial availability The functional group content fluorine polymer obtained by polymerizing in the functional group content fluorine-containing olefin obtained by this invention keeps good relations with various heat-resistant thermoplastics well, and can form a uniform distributed state.

Furthermore, the mold goods obtained by fabricating the thermoplastics constituent which consists of said polymer and said thermoplastics have a mechanical property, moldability, the outstanding heat-resisting property, and outstanding chemical resistance.

[Translation done.]